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**Chemistry.** — *Die Metastabilität der Materie und deren Bedeutung für unsere kalorimetrischen Standarde.* (Erste Mitteilung.) Von ERNST COHEN und H. GOEDHART.

(Communicated at the meeting of January 31, 1931),

*Einleitung.*

Vor etwa sechs Jahren fingen ERNST COHEN und W. J. D. VAN DOBBENBURGH<sup>1)</sup> eine Untersuchung an, welche die Ermittlung der Stabilitätsbeziehungen zwischen den verschiedenen Modifikationen der Salizylsäure bezweckte. Diese Studie setzten sie indes damals nicht fort, da während der Ausführung derselben gewisse merkwürdige Erscheinungen beobachtet wurden, welche zu einer eingehenden Untersuchung nach anderer Richtung (über den Einfluss sehr geringer Spuren Wasser auf Lösungsgleichgewichte) führten.

In der Literatur finden sich nur wenige, sehr kurze Andeutungen, welche vermuten lassen, dass die Salizylsäure in mehreren Modifikationen aufzutreten vermag. Indes rechtfertigten die Untersuchungen, welche in den letzten Jahren im *van 't Hoff-Laboratorium* über die Metastabilität der Materie ausgeführt wurden, die Auffassung, dass im Anschluss an die genannten, sehr vereinzelt Andeutungen bei eingehendem Studium sich tatsächlich der Beweis erbringen liesse, dass auch die Salizylsäure polymorph ist und sich häufig, wenn nicht immer, als metastabiles Gemisch in unseren Händen befindet.

Sollte dem tatsächlich so sein, so wäre dieser Erscheinung eine besondere Bedeutung beizulegen weil in den letzten Jahren das Verwenden dieser Substanz als (sekundären) Standard beim Eichen kalorimetrischer Systeme, speziell falls es sich um die Bestimmung von Verbrennungswärmen handelt, von vielen Seiten befürwortet worden ist. Dementsprechend haben mehrere Forscher sich in letzter Zeit mit der genauen Ermittlung der Verbrennungswärme dieser Säure beschäftigt.

Die oben erwähnten, ganz kurzen Andeutungen, welche Polymorphie der Salizylsäure vermuten liessen, ergeben sich aus folgendem:

1. A. H. RICHARD MÜLLER<sup>2)</sup> schrieb (1914) in seiner Arbeit „Ueber total instabile Formen“: „Bei der Salizylsäure ist die instabile Form stets nur für einen Augenblick sichtbar und wird sofort von der stabilen Form vernichtet.“

2. Gelegentlich einer mikroskopischen Durchmusterung von 550 organischen Präparaten der Sammlung des Marburgers Universitätslabora-

<sup>1)</sup> Verslag Akad. Wetenschappen Amsterdam **34**, 518 (1925); auch Proc. Acad. Sci Amsterdam **28**, 702 (1925); Z. physik. Chem. **118**, 37 (1925).

<sup>2)</sup> Z. physik. Chem. **86**, 77 (1914). Speziell S. 233.



toriums notierten SCHAUM, SCHÄELING und KLAUSING<sup>1)</sup> die Salizylsäure als monotrop und dimorph.

3. Zwar ergab näheres Studium der in der Literatur bisher publizierten Löslichkeitsbestimmungen der Salizylsäure in Wasser bei gegebener Temperatur, deren Ergebnisse in Tabelle 1 zusammengestellt sind, dass die Technik derselben in manchen Fällen die Kritik in hohem Masse herausfordert, doch sind die Differenzen zwischen den gefundenen Werten in den sorgfältig ausgeführten Bestimmungen so gross, dass dieselben auf die Möglichkeit der Existenz verschiedener Bodenkörper bei der nämlichen Temperatur hinwiesen.

TABELLE 1.  
Löslichkeit der Salizylsäure in Wasser (gr. pro 100 gr. Wasser) bei 25° 00 C.

Name des Autors	gr. Salizylsäure pro 100 gr. Wasser	Bemerkungen
BOURGOIN <sup>2)</sup> (1879) . . . . .	0.325	direkt gefunden
PAUL <sup>3)</sup> (1894) . . . . .	0.2261	" "
WALKER und WOOD <sup>4)</sup> (1898) .	0.224	aus einer Interpolationsformel berechnet
HOFFMANN und LANGBECK <sup>5)</sup> (1905)	0.2211 (Temp. 24° 9 C.)	direkt gefunden
KARPLUS <sup>6)</sup> (1907) . . . . .	0.2219	" "
SAVORRO <sup>7)</sup> (1912) . . . . .	0.248	" "
BAILEY <sup>8)</sup> (1925) . . . . .	0.222	aus einer Interpolationsformel berechnet

Während wir a.a.O. mehr in Einzelheiten auf die obengenannten Bestimmungen einzugehen gedenken, sei hier nur bemerkt, dass wir uns zunächst durch eigene, möglichst exakt ausgeführte, Versuche ein Bild von dem Verlauf der Löslichkeitskurve der Salizylsäure zu entwerfen bezweckten um dadurch einer eventuellen Polymorphie derselben auf die Spur zu kommen.

## DIE VERSUCHE.

### A. Die benutzten Stoffe.

1. *Salizylsäure.* In den hier zu erörternden Versuchen wurde zunächst ein Präparat „Kahlbaum für kalorimetrische Bestimmungen“ verwendet,

<sup>1)</sup> Ann. **411**, 161 (1916).

<sup>2)</sup> Ann. chim. phys. (5) **15**, 161 (1878); Bull. Soc. chim. **31** (I) 53 (1879).

<sup>3)</sup> Z. physik. Chem. **14**, 105 (1894).

<sup>4)</sup> J. Chem. Soc. **73** (II) 618 (1898).

<sup>5)</sup> Z. physik. Chem. **51**, 385 (1905).

<sup>6)</sup> Dissert. Berlin (1907).

<sup>7)</sup> Atti. Accad. Sci. Torino **48**, 948 (1913).

<sup>8)</sup> J. Chem. Soc. **127** (II) 1951 (1925).



das uns 1925 geliefert war. Da sich beim Titrieren mit einer sorgfältigst auf Bernsteinsäure und Adipinsäure eingestellten Barytlauge (Vergl. § 4.) und bei der späteren Untersuchung (siehe unten § 13) ergab, dass die Säure *chemisch* rein war, somit auch Para- und Meta-oxybenzoësäure nicht enthielt, wurde sie ohne Weiteres verwendet.

2. Das benutzte Wasser war langsam aus einem schwerverzinnnten Apparat destilliert worden; 75 cc. desselben gaben bereits mit weniger als 0.01 cc. Barylösung 0.03910 n. einen starken Umschlag mit Neutralrot, dem Indikator, den wir auch später bei der Feststellung der Konzentration der gesättigten Salizylsäurelösungen (mittels dieser Barylösung) verwendeten. Es hatte sich nämlich herausgestellt, dass dieser Indikator sich zu diesem Zwecke durch seinen äusserst scharfen Umschlag vorzüglich eignet.

### B. Die Löslichkeitsbestimmungen.

3. Da es sich, wie oben bereits gesagt wurde, um die Ausführung möglichst exakter Löslichkeitsbestimmungen handelte, verwendeten wir das von ERNST COHEN und VAN DOBBENBURGH früher<sup>1)</sup> beschriebene Verfahren. Nachdrücklich betont sei, dass wir die von niedriger Temperatur aus erreichten Lösungsgleichgewichte stets durch Bestimmungen mit übersättigten Lösungen kontrollierten. Nur wenn die von beiden Seiten erreichten Gleichgewichte innerhalb der Versuchsfehler identisch waren, wurde der gefundene Löslichkeitswert als richtig betrachtet.

Die benutzten Thermometer (BECKMANN), in  $\frac{1}{100}$  Grad geteilt, waren mit einem von der Physikalisch-Technischen Reichsanstalt, Charlottenburg-Berlin, untersuchten Instrumente verglichen worden. Die Temperaturschwankungen während der Darstellung der gesättigten Lösungen betrugen weniger als  $\frac{1}{100}$  Grad.

### C. Die Analyse der gesättigten Lösungen.

4. Die verwendeten Büretten und Messkolben wurden in bekannter Weise geeicht, unser Gewichtssatz nach dem TH. W. RICHARDSSchen Verfahren<sup>2)</sup>. Wie bereits oben angedeutet, erfolgte die Konzentrationsbestimmung der gesättigten Lösungen durch Titrieren mittels einer (0.03910 n.) Barylösung, welche auf reinste Bernsteinsäure und Adipinsäure<sup>3)</sup> eingestellt war.

0.1258 gr. Salizylsäure erforderten 23.29 cc. dieser Barylösung (Indikator Neutralrot). Hieraus ergibt sich für das Molgewicht der Salizylsäure 138.1.

Berechnet für  $C_7H_6O_3$ : 138.05.

In unseren Versuchen bei 25° 00 C. verwendeten wir etwa 40 gr. der gesättigten Lösungen, in denen bei 0° 0 C. etwa 100 gr. derselben. Die

<sup>1)</sup> Verslag Akad. Wetenschappen Amsterdam, **34**, 518 (1925); auch Proc. Acad. Sci. Amsterdam **28**, 702 (1925); Z. physik. Chem. **118**, 37 (1925).

<sup>2)</sup> Z. physik. Chem. **33**, 605 (1900).

<sup>3)</sup> Vergl. F. TH. VAN VOORST, Chem. Weekblad **25**, 22 (1928).

Wägungen der 40 gr. fanden auf einer BUNGESchen Wage bis auf 0.5 mgr. statt, die von 100 gr. auf einer grösseren Wage auf 20 mgr. genau. Sämtliche Wägungen wurden auf das Vakuum reduziert.

#### D. Die ersten Löslichkeitsversuche.

5. Zu unseren ersten Versuchen kam als Bodenkörper die *ohne Weiteres* der Standflasche entnommene kristallinische Substanz zur Verwendung; dieselbe war *nicht* zerrieben.

Die so erhaltenen Ergebnisse sind in Tabelle 2 zusammengestellt.

TABELLE 2.  
Temperatur 25°.00 C.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
2	15	0.2242
3	18	0.2235
7	12	0.2265
12	2	0.2266

6. Da die gefundenen Werte sehr weit auseinander gehen, wurde an die Möglichkeit gedacht, dass die Bodenkörper in den verschiedenen Schüttelflaschen in sehr verschiedener Zerteilung vorhanden sein könnten. Bekanntlich ist die Löslichkeit eines Stoffes c.p. bei sehr weitgehender Zerteilung eine grössere als bei gröberer. Wir entschlossen uns somit in neuen Versuchen in allen Flaschen *dasselbe* Material zu verwenden, nachdem es im Achatmörser sehr fein gepulvert worden war. Sollte tatsächlich der Korngrösse der Salizylsäure eine Rolle zukommen, so wären dann Löslichkeiten zu erwarten, welche entweder den höchstgefundenen Wert oder einen noch höheren aufweisen müssten. Tabelle 3 enthält die diesbezüglichen Versuchsdaten:

TABELLE 3.  
Temperatur 25°.00 C.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
16	2	0.2232
17	2	0.2226
18	21	0.2233
19	21	0.2226

Mittel . . . 0.222<sup>9</sup>

Da die Löslichkeit weder den in Tabelle 2 angegebenen höchsten Wert erreicht, noch einen höheren aufweist, sondern in allen Fällen einen weit



niedrigeren, so ist zu schliessen, dass es sich hier um eine Stabilisierung des ursprünglichen Bodenkörpers infolge des Pulverens im Mörser handelt. Derartige Fälle sind bereits häufiger konstatiert worden. Allgemein bekannt ist der Fall des unterhalb  $127^{\circ}\text{C}$ . metastabilen gelben  $\text{HgJ}_2$ , welches sich bei gewöhnlicher Temperatur durch Reiben momentan in die stabile, rote Modifikation umwandelt, sowie der des explosiven Antimons, welches sich bereits bei ganz leiser Berührung stabilisiert<sup>1)</sup>. Ferner fanden SCHLEEDE und GANTZCKOW<sup>2)</sup>, dass Zinksulfid (Wurtzit) sich beim Zerdrücken im Mörser in die bei gewöhnlicher Temperatur stabile Modifikation (Blende) umwandelt, was sich an Röntgenaufnahmen der beiden Materialien feststellen liess.

Hat somit durch Reiben eine Stabilisierung unserer, ohne Weiteres der Standflasche entnommenen, Säure stattgefunden, so ist dieselbe als eine reine metastabile Form der Säure, bezw. als ein Gemisch von dieser mit stabiler Säure anzusprechen.

#### E. Die metastabile Modifikation der Salizylsäure

7. Handelt es sich nunmehr darum die Löslichkeit der metastabilen Modifikation zu ermitteln, so ist darauf zu achten, dass man der Säure während der Sättigung möglichst wenig Gelegenheit bietet sich zu stabilisieren, d.h. also, dass man die Sättigungszeit möglichst kurz wählt, dennoch dafür Sorge tragend dass völlige Sättigung erreicht wird. Zunächst wählten wir deshalb als Sättigungszeit 4 Stunden und erhielten mit dem Präparat, welches ohne Weiteres unserer Standflasche entnommen war, die in Tabelle 4 verzeichneten Werte.

TABELLE 4.  
Temperatur  $25^{\circ}\text{C}$ .

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
60*	4	0.2262
61*	4	0.2262
62	4	0.2267
88	4	0.2262
90	4	0.2270
112	4	0.2262
113	4	0.2262

Mittel . . . 0.226<sup>4</sup>

<sup>1)</sup> ERNST COHEN und W. E. RINGER, Z. physik. Chem. **47**, 1 (1904); ERNST COHEN, E. COLLINS u. TH. STRENGERS, Z. physik. Chem. **50**, 291 (1904); ERNST COHEN u. TH. STRENGERS, Z. physik. Chem. **52**, 129 (1905); ERNST COHEN u. C. C. COFFIN, Z. physik. Chem. A **149**, 417 (1930).

<sup>2)</sup> Z. Physik **15**, 184 (1923).



Die Bezeichnung \* in dieser Tabelle und den folgenden bedeutet, dass die betreffende Lösung vor dem Schütteln übersättigt war; das Gleichgewicht wurde somit von beiden Seiten erreicht.

8. Dass der betreffende Bodenkörper seine Metastabilität auch während längerer Schüttelzeiten beibehält, ergibt sich aus Tabelle 5, in der es sich ebenfalls um Salizylsäure handelt, welche ohne Weiteres der Standflasche entnommen, die aber während viel längerer Zeiten mit dem Lösungsmittel geschüttelt worden war.

TABELLE 5.  
Temperatur 25°.00 C.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
23	18	0.2264
24	18	0.2268
25	18	0.2268
26	18	0.2264
29	17	0.2265
30	17	0.2264
38	22	0.2267
57	120	0.2263
Mittel . . .		0.2265

9. Zu Versuch 57 ist Folgendes zu bemerken: In diesem kam der Bodenkörper aus Versuch 38 zur Verwendung nachdem die gesättigte Lösung von demselben entfernt worden und frisches Wasser aufgegossen war. Dieser Versuch lehrt, dass der betreffende metastabile Bodenkörper selbst nach  $22 + 120 = 142$  Std. sich noch nicht stabilisiert hat, ein Beweis wie stark diese Verzögerungserscheinungen bei der Salizylsäure zu Tage treten.

Ausserdem aber zeigt dieser Versuch, dass in sämtlichen Bestimmungen der Tabellen 4 und 5 stets eine genügende Menge der metastabilen Form im Bodenkörper zugegen war um die Löslichkeit derselben zu ergeben.

10. Es ist hier am Platze die Erscheinungen zu erörtern, welche häufig bei der Löslichkeitsbestimmung der metastabilen Säure auftreten und welche sich aus Tabelle 6 ergeben. In diesen Versuchen kam die Säure, nachdem sie ohne Weiteres der Standflasche entnommen war, zur Verwendung.

Wie aus der Tabelle 6 ersichtlich ist, können sowohl nach kürzerer (4 Std.) wie nach längerer (120 Std.) Sättigungszeit Werte gefunden wer-

TABELLE 6.  
Temperatur 25°.00 C.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
31	46	0.2253
32	46	0.2253
56	120	0.2228
58	120	0.2242
63	4	0.2248
65	18 (Bodenk. v. Versuch 63)	0.2235
127	4 (Bodenk. v. Versuch 112. Vergl. Tab. 4)	0.2234

den, welche zwischen den Löslichkeiten der metastabilen und der stabilen Modifikation liegen.

Diese Tatsache lässt sich unschwer erklären: Wird ein überschüssiges Gemisch der metastabilen und stabilen Modifikation mit reinem Lösungsmittel zusammengebracht und bei gegebener Temperatur geschüttelt, so werden beide in Lösung gehen. Findet die Sättigung mit grösserer Geschwindigkeit statt als die Umwandlung der metastabilen Modifikation in die stabile, so wird sich eine in Bezug auf die metastabile (löslichere) Modifikation gesättigte Lösung bilden: man findet dann die Löslichkeit der metastabilen Modifikation bei der betreffenden Temperatur.

Bei fortgesetztem Schütteln wird die Stabilisierung des Bodenkörpergemisches fortschreiten. Hat sich die ganze vorhandene Menge der metastabilen Form in die stabile umgewandelt, so ist die Lösung (in Bezug auf Letztere) übersättigt und, abhängig von dem Werte ihrer Kristallisationsgeschwindigkeit wird die gelöste Substanz aus der übersättigten Lösung mit grösserer, bezw. geringerer Geschwindigkeit auskristallisieren.

Nun ist bereits seit langem bekannt<sup>1)</sup>, dass Salizylsäurelösungen sehr hartnäckige Uebersättigungserscheinungen aufzuweisen vermögen. Dementsprechend wird es von den Schüttelzeiten abhängen, nach Ablauf welcher man die Lösung der Analyse unterwirft, welchen Wert man dann für deren Konzentration findet. Es handelt sich unter diesen Verhältnissen selbstverständlich nicht um die wahre Löslichkeit der betreffenden Substanz sondern um einen Zufallswert. Wie die Tabelle 6 dementsprechend dartut, können diese Werte nur zwischen der wahren Löslichkeit der stabilen und der der metastabilen Modifikation liegen.

<sup>1)</sup> OST, J. prakt. Chem. N.T. 17, 228 (1878); Auch TH. PAUL, Z. physik. Chem. 14, 104 (1894); Speziell daselbst S. 112, auch Fussnote.

*F. Die stabile Modifikation der Salizylsäure.*

11. Es wurde oben (§ 6) bereits mitgeteilt, dass Reiben im Mörser die metastabile Säure in die stabile umwandelt. Inzwischen ist es möglich, dass bei diesem Vorgange die metastabile Form sich nicht quantitativ stabilisiert; dies wird sich darin zeigen, dass mit solchem Material ausgeführte Löslichkeitsbestimmungen zunächst eine etwas grössere Löslichkeit vortäuschen, welche aber ihren normalen Wert erreicht, falls man den bei dieser Bestimmung benutzten Bodenkörper aufs neue mit frischem Lösungsmittel schüttelt.

Unsere Tabelle 7 enthält die nötigen Belege.

TABELLE 7.  
Temperatur 25°.00 C.

Versuchsnummer	1e Schüttelzeit in Stunden	Konz. in gr. pro 100 gr. Wasser	2e Schüttelzeit in Stunden	Löslichkeit in gr. pro 100 gr. Wasser	3e Schüttelzeit in Stunden	Löslichkeit in gr. pro 100 gr. Wasser
71	4	0.2241	16 $\frac{1}{2}$	0.2230	—	—
72	4	0.2243	16 $\frac{1}{2}$	0.2227	—	—
73*	4	0.2242	16 $\frac{1}{2}$	0.2230	16 $\frac{1}{2}$	0.2231
74*	4	0.2246	16 $\frac{1}{2}$	0.2232	16 $\frac{1}{2}$	0.2226
85	16	0.2233	16 $\frac{1}{2}$	0.2233	—	—
86	16	0.2232	16 $\frac{1}{2}$	0.2233	—	—
114	4	0.2240	16	0.2226	—	—
115	4	0.2235	16	0.2228	—	—

12. Dass aber auch häufig blosses Reiben die völlige Stabilisierung herbeizuführen im Stande ist, beweisen die Zahlen unserer Tabelle 8, in welcher es sich um Präparate handelt, welche sofort nach dem Reiben die Löslichkeit der stabilen Modifikation ergaben, wie dies übrigens auch in den Versuchen 85 und 86 der Tabelle 7 der Fall war.

TABELLE 8.  
Temperatur 25°.00 C.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
33	46	0.2234
35	46	0.2228
36	46	0.2231
59	120	0.2232



Das Gesamtmittel aus den wahren Löslichkeitswerten für die stabile Modifikation bei 25°.00 C., welches wir den Tabellen 7 und 8 entnehmen, ist somit 0.223<sup>0</sup> gr. pro 100 gr. Wasser.

### G. Die chemische Reinheit unserer Säure.

13. Oben (§ 4) wurde bereits dargetan, dass die von uns verwendete Säure tatsächlich der Formel  $C_7H_6O_3$  entspricht. Es handelte sich nunmehr noch darum den Nachweis zu erbringen, dass dieselbe frei von ihren sehr viel löslicheren Isomeren war<sup>1)</sup>. Unsere Versuche 85 und 86 (Tabelle 7) sowie 128 und 129 (Tabelle 11) erbringen diesen Beweis, da sie ergaben, dass unsere völlig stabilisierte Säure in nachfolgenden Löslichkeitsbestimmungen (in welchen jedesmal frisches Lösungsmittel zur Verwendung kam), identische Werte für die Löslichkeit lieferte.

### H. Löslichkeitsversuche bei 0°.0 C.

14. Zwecks Erhärtung des oben Mitgeteilten führten wir ganz analoge Versuche bei 0°.0 C. aus. Die Flaschen wurden in einem Thermostaten geschüttelt, welcher mit Wasser und feingestossenem Eis gefüllt war. Die Ergebnisse der mit der metastabilen Säure ausgeführten Versuche sind in Tabelle 9, die der mit der stabilen ausgeführten in Tabelle 10 zusammengefasst.

TABELLE 9.  
Temperatur 0°.0 C. Metastabile Modifikation.

Versuchsnummer	Schüttelzeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
66	8	0.0950
67	8	0.0949
68*	8	0.0948
69*	8	0.0944
Mittel . . .		0.094 <sup>8</sup>

### I. Stabilisierung durch Erwärmen.

15. Sind die oben gefundenen Daten und die darauf sich stützenden Ueberlegungen richtig, so musste es möglich sein die metastabile Modifikation (das metastabile Gemisch) welche(s) unser Standardpräparat bildet, in trockenem Zustande durch Temperaturerhöhung zu stabilisieren. Da wir noch nicht wissen, ob die beiden Modifikationen der Salizylsäure im Verhältnis der Enantiotropie oder der Monotropie zu einander stehen, blieb die Wahl der anzuwendenden Stabilisierungstemperatur vorläufig eine ziemlich willkürliche. Wir wählten 75° C. da wir die Säure, zwecks Vorbeugung

<sup>1)</sup> Vergl. WALKER und WOOD J. Chem. Soc. 73 (II) 618 (1898).

TABELLE 10.  
Temperatur 0.°0 C. Stabile Modifikation.

Versuchs- nummer	1e Schüttel- zeit in Stunden	Konz. in gr. pro 100 gr. Wasser	2e Schüttel- zeit in Stunden	Löslichkeit in gr. pro 100 gr. Wasser	3e Schüttel- zeit in Stunden	Löslichkeit in gr. pro 100 gr. Wasser
40	4	0.0922	—	—	—	—
41	4	0.0921	—	—	—	—
42	5	0.0923	—	—	—	—
43*	5	0.0918	—	—	—	—
45	4	0.0925	—	—	—	—
47	4	0.0917	—	—	—	—
51	3	0.0927	—	—	—	—
54	5	0.0923	—	—	—	—
55	5	0.0929	—	—	—	—
119	5	0.0926	5	0.0911	5	0.0913
120	5	0.0929	5	0.0916	5	0.0919
121	5	0.0931	5	0.0916	5	0.0909
122	5	0.0934	5	0.0921	5	0.0918

Als Mittelwert nach zweimaligem Schütteln ergibt sich hieraus für die Löslichkeit der stabilen Modifikation bei 0°.0 C. der Wert **0.0916**, nach dreimaligem Schütteln der Wert **0.0915**.

Es treten also auch bei 0° C. zwei verschiedene Modifikationen der Salizylsäure auf.

chemischer Zersetzung, nicht zu hoch erhitzen wollten. Dementsprechend erwärmten wir die ohne Weiteres der Standflasche entnommene Säure während verschiedener Zeiten im elektrischen Trockenschrank auf 75° C. und ermittelten sodann deren Löslichkeit bei 25°.00 C.

Die Tabelle 11 enthält die Versuchsergebnisse.

TABELLE 11.  
Stabilisierung der metastabilen Salizylsäure bei 75° C.  
Löslichkeitsbestimmung bei 25°.00 C.

Versuchs- nummer	Dauer der Stabilisierung i. Std.	1e Schüttel- zeit in Stunden	Konz. in gr. pro 100 gr. Wasser	2e Schüttel- zeit in Stunden	Lösl. in gr. pro 100 gr. Wasser
79	120	16½	0.2258	—	—
80	120	16½	0.2247	—	—
128	408	4	0.2227	16	0.2227
129	408	4	0.2227	16	0.2229

Diese Tabelle zeigt aufs Schlagendste wie langsam die Stabilisierung der Säure in völlig trockenem Zustande vor sich geht. Wir finden hier auch die Erklärung für die Tatsache, dass die sich während etwa 6 Jahren in unserer Standflasche bei Zimmertemperatur befindliche Säure sich in dieser Zeit nicht völlig stabilisiert hat.

#### K. Die Darstellung der verwendeten Säure.

16. Auf Anfrage teilte die Firma KAHLBAUM, Berlin, uns freundlichst mit, dass die Säure „einer mehrfachen Reinigung durch Sublimation unterworfen wird“. Bekanntlich<sup>1)</sup> ist Sublimieren eines der Verfahren, welche zur Darstellung *chemisch* reiner Stoffe verwendet werden und die gerade zur Bildung metastabiler Modifikationen, bezw. zu Gemischen derselben mit stabilen führen können.

#### L. Die Salizylsäure als Standardsubstanz in der Kalorimetrie.

17. Wie oben (Einleitung) bereits betont wurde, ist diese Säure in den letzten Jahren besonders von P. E. VERKADE und J. COOPS JR.<sup>2)</sup> als Ursubstanz (sekundärer Standard) zur Eichung von kalorimetrischen Systemen empfohlen worden. Es ist aus diesem Grunde, dass mehrere chemische Fabriken ein spezielles Präparat zu diesem Zwecke (manchmal mit Angabe der Verbrennungswärme pro Gramm Substanz) in den Handel bringen.

Das von uns hier studierte, *chemisch* reine Material (vergl. § 13) besteht, wie die Versuche gelehrt haben, nicht aus einer einzigen Modifikation, sondern aus einem metastabilen Gemisch zweier Modifikationen. Die Zusammensetzung dieses Gemisches kann sich, abhängig von äusseren Verhältnissen (Reibung, Temperatur, Feuchtigkeit) im Laufe der Zeit ändern. Da es sich hier also um ein *physikalisch* unreines Objekt handelt, liegt es nunmehr auf der Hand, dass eine Bestimmung der Verbrennungswärmen beider *physikalisch* und *chemisch* reinen Modifikationen der Salizylsäure not tut um festzustellen, wie gross deren Unterschied ist und damit die Frage beantworten zu können, ob die Umwandlungswärme einen Einfluss auf den Wert der Verbrennungswärme zu üben im Stande ist, falls man Gemische beider Modifikationen in Händen hat.

18. Inzwischen sei bemerkt, dass bei den bisherigen Bestimmungen der Verbrennungswärme die benutzte Säure wohl immer vor dem Versuch zerrieben wurde da man dieselbe meist in Pastillenform verwendet, so dass es wahrscheinlich ist, dass das untersuchte Material infolgedessen nur eine geringe Menge der metastabilen Modifikation enthielt. Wie dem auch sei, es wird in Zukunft auf grund unserer Versuche stets möglich sein die stabile

<sup>1)</sup> Vergl. ERNST COHEN, Physikalisch-chemische Metamorphose, Leipzig 1927, Seite 56 ff. wo sich auch Literaturangabe befindet. Auch Englisch: Physico-chemical Metamorphosis, New-York und London, 2e Aufl. 1928 S. 86 ff.

<sup>2)</sup> Rec. Trav. chim. **43**, 561 (1924).



Modifikation der Salizylsäure als Ursubstanz kalorimetrischen Messungen zu grunde zu legen.

### *Zusammenfassung.*

1. Es wurde mittels exakter Löslichkeitsbestimmungen der Nachweis geführt, dass die Salizylsäure bei gewöhnlicher Temperatur in zwei Modifikationen aufzutreten vermag und dass die metastabile Form sehr hartnäckig (jahrelang) als solche existenzfähig ist.

2. Es lassen sich auf Grund der gewonnenen Erfahrungen die grossen Abweichungen erklären, die zwischen den Löslichkeitsbestimmungen mancher Autoren vorliegen.

3. Infolge der hartnäckigen Metastabilität, welche die Säure aufzuweisen vermag, können Präparate, welche als Eichsubstanz kalorimetrischer Systeme benutzt werden, als undefinierte, metastabile Gemische bestehen bleiben, deren Verbrennungswärme sich durch äussere Verhältnisse wie Reiben, Erwärmen, Feuchtigkeit, im Laufe der Zeit ändern. Eine genaue Bestimmung der Verbrennungswärmen der beiden *physikalisch* und *chemisch* reinen Modifikationen tut not um festzustellen, in wiefern die bisher für die Salizylsäure ermittelte Verbrennungswärme sich als Eichwert verwenden lässt. Herr Kollege P. E. VERKADE in Rotterdam hat sich freundlichst bereit erklärt die betreffenden kalorimetrischen Bestimmungen auszuführen.

Utrecht, im Januar 1931.

VAN 'T HOFF-Laboratorium.

**Chemistry.** — *On the Allotropism of Rhodium and on Some Phenomena observed in the X-ray-Analysis of heated Metal-Wires.* By F. M. JAEGER and J. E. ZANSTRA.

(Communicated at the meeting of January 31, 1931).

§ 1. In a previous and the next paper<sup>1)</sup> it has been demonstrated, that the  $c_p$ — $t$ -curves for *palladium* at about 1530° C. and for *rhodium* somewhere in the neighbourhood of 1200° C., doubtlessly show a *maximum*, which in the case of *rhodium* is even a very steep one. In connection with an apparent change of volume observed at temperatures exceeding 1200° C., in the crucible containing the *rhodium*, suspicion arose, that under these circumstances some structural change of the enclosed metal had taken place. The following experiments were, in both cases, executed with the purpose of elucidating these phenomena observed by means of an elaborated X-ray-analysis. In the course of these investigations, we met, however, with some particular phenomena, and, therefore, we extended our experiments, including also *platinum* within this series. In the present paper a review is given of the results obtained during these studies.

In the case of the metals mentioned it hitherto appeared impossible to state the occurrence of a transition-temperature; all their physical properties in their dependance on the temperature rather seem to vary in a perfectly *continuous* way. Neither is there in literature, — for instance in the case of *rhodium*, — any indication to be found of an abrupt change in the behaviour of this metal: thus, HOLBORN and WIEN, WAIDNER and BURGESS, DAY and SOSMAN<sup>2)</sup> and many other investigators working with *rhodium* and its alloys, — they all found a *continuous* change of its physical properties with the temperature. We, in our previous paper, were able to state the same fact, although some peculiarities in the shape of the curves representing the change of the temperature-coefficient of the electrical resistance (turning-point between 1100° and 1200° C.) doubtlessly seem to indicate, that some change in the internal structure of the metal occurs. In the case of *palladium* and *platinum*, however, even these indications proved to be absent, and also X-ray-analysis failed to prove

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<sup>1)</sup> F. M. JAEGER and E. ROSENBOHM, *Proceed. R. Acad. of Sciences Amsterdam*, **33**, (1930), p. 457; **34**, (1931), p. 85.

<sup>2)</sup> L. HOLBORN and W. WIEN, *Ann. d. Phys.*, **47**, (1892), 107; G. WAIDNER and K. BURGESS, *Bull. Bur. of Standards*, **3**, (1907), 200; A. L. DAY and R. B. SOSMAN, *CARNEGIE-Publ.* **157**, Washington, (1911), 120; A. L. DAY and L. HOLBORN, *Ann. der Phys.*, **2**, (1900), 522; *Amer. Journ. of Science*, (4), **8**, (1899), 303.

the existence of other modifications of these metals. Notwithstanding this, on heating, they showed the same phenomena as those first stated in the case of *rhodium*.

## § 2. *Rhodium*.

If finely divided metallic *rhodium*, such as it may be obtained by the reduction of its salts in alkaline solution by means of hydrazine-hydrate, etc., is, without previous heating, examined by means of X-rays after DEBIJE-HULL's method, powder spectrograms are obtained, the diffraction-lines of which are very broad and hazy, reminding those of colloidal substances. At first sight they seem to be in agreement with the presence of a face-centred cubic lattice, the parameter  $a_0$  of it having somewhat variable values, ranging from 3.77 Å. to 3.80 Å. Tentatives were made to obtain the metal in somewhat coarser grains, without heating it. With this purpose solutions of the chloride:  $Na_3Rho Cl_6$ , were electrolysed between a carbon-anode and a *rhodium*-cathode with a voltage of 2.5 Volts and a current-density of about 1.2 Amp. pro  $cm^2$ . The metal is slowly deposited in the form of darkly coloured clumps, which, under the microscope, have the appearance of cubes with rounded edges and curved facets, which are striated in three perpendicular directions; but no well developed crystals ever were obtained. The diffraction-lines of this product were no better than those mentioned before. A better product is obtained in the form of a greyish, brittle mass, if, instead of the chloride, the complex oxalate:  $K_3\{Rho (C_2O_4)_3\} + 4\frac{1}{2} H_2O$  in very weakly acid solution, is subjected to electrolysis, with a current-density of about 3 Amp. pro  $cm^2$ . Even in this case, however, no good crystals were obtained. The finest powder obtained by grinding the product in a mortar, was used for X-ray-examination, and thus some better spectrograms, as well with copper-, as with iron-radiation were obtained, which, besides some stronger lines, showed a great number of much fainter ones. Later-on it was stated, that these spectrograms were identical with those obtained with the best product deposited from the chloride; also, that a heating at 1000° C. did not appreciably alter the character of the spectrograms. If, however, the powder, wrapped in platinum-foil, was heated for a long time at 1500° C. and then suddenly quenched, the obtained spectrogram was completely identical with that of the metal in wire-form, which afterwards will be described.

The results of the X-ray-analysis of the powder not previously heated, are collected in Table I; they were obtained by means of iron- and copper-radiation; the spectrograms produced by using a copper-target were practically identical with those obtained with iron-radiation; but occasionally they showed a greater number of faint lines than the latter ones.

Even, if the lines which practically coincide with those of the face-centred cubic form, are left apart, at least 39 lines remain, which cannot be accounted for in that lattice and which must be attributed to another modification, which is the stabler one at lower temperatures, and which



TABLE I.  
Powder-Spectrograms of electrolytically deposited Rhodium.

N <sup>o</sup> . of line:	2l in mm.:	Int.:	$\lambda$ :	$\theta$ :	$\sin^2 \theta$ (observed):	$\sin^2 \theta$ (calculated):	$\Sigma$ :	Indices $\{h\ k\ l\}$ :
1	× 32.92	1	$\alpha$	10° 37'	0.0339	0.0331	3	(111)
2	37.88	3	$\alpha$	12 12	0.0477	0.0442	4	(200)
3	45.84	2	$\alpha$	14 48	0.0652	0.0663	6	(211)
4	× 53.19	2	$\alpha$	17 10	0.0871	0.0884	8	(220)
5	× 56.76	2	$\alpha$	18 19	0.0988	0.0995	9	(221) ; (300)
6	× 59.95	2	$\alpha$	19 20	0.1096	0.1105	10	(310)
7	62.15	2	$\beta$	20 3	0.1176	0.1178	13	(320)
8	65.81	3	$\alpha$	21 14	0.1312	0.1326	12	(222)
9	68.66	4	$\alpha$	22 9	0.1422	0.1436	13	(320)
10	74.39	2	$\beta$	24 0	0.1654	0.1658	(15)	$\beta$ (111) of $\beta$ -Modif.
								—
11	77.62	1	$\alpha$	25 3	0.1792	0.1768	16	(400)
12	81.86	5	$\alpha$	26 25	0.1979	0.1989	18	$\alpha$ (111) of $\beta$ -Modif.
								(330) ; (411)
13	87.10	2	$\alpha$	28 6	0.2219	0.2210	20	$\beta$ (200) of $\beta$ -Modif.
								(420)
14	× 89.27	1	$\alpha$	28 48	0.2321	0.2320	21	(421)
15	× 91.35	1	$\alpha$	29 28	0.2419	0.2431	22	(332)
16	96.15	3	$\alpha$	31 1	0.2655	0.2652	24	(422)
17	99.10	1	$\alpha$	31 58	0.2803	0.2762	25	$\alpha$ (200) of $\beta$ -Modif.
								(430) ; (500)
18	× 102.01	2	$\alpha$	32 55	0.2953	0.2983	27	(333) ; (511)
19	× 107.65	2	$\alpha$	34 44	0.3246	0.3204	29	(432) ; (520)
20	108.92	3	$\alpha$	35 8	0.3312	0.3315	30	(521)
21	113.57	3	$\alpha$	36 38	0.3558	0.3536	32	(440)
22	119.27	1	$\alpha$	38 29	0.3872	0.3867	35	(531)
23	121.10	2	$\alpha$	39 4	0.3972	0.3978	36	(600)
24	× 125.35	1	$\alpha$	40 26	0.4206	0.4199	38	(532) ; (611)
25	127.49	3	$\beta$	41 8	0.4327	0.4310	(39)	$\beta$ (200) of $\beta$ -Modif.
								—
26	× 132.17	1	$\alpha$	42 26	0.4554	0.4531	41	(540) ; (621)
27	× 141.47	1	$\alpha$	45 33	0.5095	0.5083	46	(631)
28	× 143.05	4	$\alpha$	46 9	0.5201	0.5190	(47)	—
						0.5232		$\alpha$ (220) of $\beta$ -Modif.

TABLE I (Continued).  
Powder-Spectrograms of electrolytically deposited Rhodium.

N <sup>o</sup> . of line:	2l in mm.:	Int.:	$\lambda$ :	$\theta$ :	$\sin^2 \theta$ (observed):	$\sin^2 \theta$ (calculated):	$\Sigma$ :	Indices $\{h k l\}$ :
29	145.50	4	$\alpha$	46°57'	0.5340	0.5304	48	(444)
30	148.90	2	$\alpha$	48 3	0.5531	0.5525	50	(543) ; (505) ; (710)
31	152.72	2	$\alpha$	49 16	0.5742	0.5746	52	(640)
						0.5920	←	$\beta$ (311) of $\beta$ -Modif.
32	158.34	2+	$\beta$	51 4	0.6053	0.6077	(55)	—
33	162.02	1	$\alpha$	52 17	0.6257	0.6298	57	(544) ; (722)
34	×165.30	2	$\alpha$	53 20	0.6434	0.6409	58	(730)
						0.6468	←	$\beta$ (222) of $\beta$ -Modif
35	167.79	2+	$\beta$	54 8	0.6568	0.6520	59	(731) ; (553)
36	173.0	1	$\alpha$	55 49	0.6842	0.6851	62	(732)
37	177.0	3	$\alpha$	57 6	0.7050	0.7072	64	(800)
38	×179.2	6	$\alpha$	57 49	0.7163	0.7182	65	(740) ; (810)
						0.7191	←	$\alpha$ (311) of $\beta$ -Modif.
39	×181.1	5	$\alpha$	58 25	0.7257	0.7293	66	(554) ; (741) ; (811)
40	183.72	1	$\alpha$	59 17	0.7391	0.7404	67	(732)
41	188.1	2	$\alpha$	60 40	0.7600	0.7625	69	(742) ; (821)
42	190.54	3	$\alpha$	61 28	0.7718	0.7735	70	(653)
						0.7818	←	$\alpha$ (222) of $\beta$ -Modif.
43	193.10	4	$\alpha$	62 18	0.7839	0.7955	72	(660) ; (822)
44	×198.69	1	$\alpha$	64 6	0.8092	0.8067	73	(830)
45	×199.80	1	$\alpha$	64 28	0.8140	0.8177	74	(743) ; (750) ; (831)
46	×202.63	1	$\alpha$	65 22	0.8263	0.8288	75	(555) ; (751)
47	×204.50	1	$\alpha$	65 58	0.8341	0.8398	76	(662)
48	208.61	2	$\alpha$	67 18	0.8510	0.8508	77	(654) ; (832)
49	211.50	2	$\beta$	68 14	0.8625	0.8619	78	(752)
						0.8616	←	$\beta$ (400) of $\beta$ -Modif.
50	220.48	2	$\alpha$	71 8	0.8954	0.8950	81	(744) ; (841)

The values of 2l are the mean values of four series of measurements with the comparator.

$R = 44.4$  mm. Exposure: 60—96 m. Amp. hours. Iron-anticathode.

Quadratic Equation:  $\sin^2 \theta = 0.01105 \cdot (h^2 + k^2 + l^2)$ . ( $\alpha$ -radiation).

$\sin^2 \theta = 0.00906 \cdot (h^2 + k^2 + l^2)$ . ( $\beta$  radiation).

Simple cubic lattice, with ;  $a_0 = 9.211 \text{ \AA.} \pm 0.09$ .

occurs *besides* the ordinary form of the metal<sup>1)</sup>; we will indicate it as the  $\alpha$ -modification of the metal<sup>2)</sup>. There is no doubt, however, that simultaneously also the ordinary  $\beta$ -form of the metal is present, and that, therefore, the product examined is a *mixture* of the two. This must be concluded from the fact, that in the spectrogram the lines No. 10, 25, 28 and 32 correspond to a sum of squares of the indices equal to 15, 39, 47 and 55 respectively, — which cannot be accounted for in any other way, than by assuming that they belong to the  $\beta$ -modification itself. Also the other lines of this modification are met with exactly at or very nearly at the positions of the lines 12, 13, 17, 35, 38, 43 and 49, — from which they hardly can be separated, because they cause a broadening of the adjacent lines and an apparent increase of their intensities. From the rather weak intensities of these lines of the  $\beta$ -modification in comparison with those of the pure modification itself, it can be concluded that the amount of the  $\beta$ -modification in the mixture obtained by electrolysis, is only a rather moderate one<sup>3)</sup>. The fact that all the lines mentioned practically coincide with those of the  $\alpha$ -modification, also gives a rational explanation of the phenomenon of the hazy and broadened aspect of the lines of the spectrograms obtained from the *rhodium*-powder first studied in this way. Partially this hazy aspect is doubtlessly also caused by the semi-colloidal state of the particles: a rough estimation from the broadness of the lines taught us, that the particles must have a linear dimension of about 300 Å; which means, that they consist of about 33 atoms arranged along each edge of the cubic particles. Also the phenomenon of the occasional occurrence of some multiple lines in the spectrograms at ordinary temperature is explained by this character of the preparations studied, as *mixtures* of the  $\alpha$ - and  $\beta$ -modifications together.

The  $\alpha$ -modification is, like the  $\beta$ -modification, cubic, but it has a simple cubic lattice with an edge of 9.211 Å. The number of atoms pro elementary cell can be estimated from the density of the preparation:

with 48 atoms in the cell,  $d$  must be 10.427;

with 32 atoms in the cell,  $d$  must be 6.951;

with 96 or 64 atoms in the cell,  $d$  must be twice the first or the second number respectively.

Bij four independant direct measurements with three different preparat-

<sup>1)</sup> A spectrogram of a *rhodium-oxide*, presumably  $RhO_3O_4$ , which was prepared from the hydrate by heating it at 900° C., showed 27 lines, which as well with respect to their location as to their relative intensities, did *not* coincide with the lines here observed. An admixture of an oxide to the metal obtained by cathodical reduction being beforehand highly improbable, this control leaves no doubt as to the fact, that the lines observed are *not* produced by the presence of rhodium-oxide.

<sup>2)</sup> By comparison with the spectrogram of  $\alpha$ -iron, we have, moreover, ascertained ourselves, that these lines *cannot* correspond to the presence of traces of iron, -the only imaginable impurity of the preparation.

<sup>3)</sup> About 12 %.



ions, we found the density to be: 10.68 at 20° C.; therefore, the number of atoms in the elementary cell of  $\alpha$ -rhodium must be *fourty-eight*.

If to these 48 atoms in the cubic cell a forty-eight-fold position (with 3 parameters  $x, y, z$ ) shall be attributed, the  $\alpha$ -modification only can belong to one of the four space-groups:  $O_h^1$ ,  $O_h^2$ ,  $O_h^3$  or  $O_h^4$ . The uncertainty in the estimated relative intensities of the rather faint lines of the spectrograms does, at this moment, not allow us to decide, which of these four groups is the right one.

The  $\alpha$ -modification seems to be stable besides the  $\beta$ -form, however, within a range of temperatures at least extending as high as 1000° C., always, however, diminishing in quantity, as the temperature increases.

§ 3. In contrast to this  $\alpha$ -modification, the ordinary form of the metal is the face-centred cubic one, with a parameter  $a_0$  having the value: 3.791 Å. The results obtained with a thin wire of the metal at room-temperature are collected in Table II, copper-radiation being used in these experiments. The occurrence of the lines 1, 6 and 20 proves, that somewhat of the other modification still is present, which also may be concluded from the fact, that the data for the specific weight of the compact metal, as given in literature, are rather variable. The lines 17 and 19 have the character of narrow doublets. The results obtained by means of iron radiation, as well in the case that the wire was rotated about its axis, as when it remained unmoved, were completely analogous to those mentioned. They are in agreement with the data previously published by other investigators <sup>1)</sup>.

§ 4. After this we proceeded to the study of the influence which heating has on the structure of the metal. A drawn wire of purest rhodium <sup>2)</sup>, with a diameter of 0.3 mm and a length of 35 mm was fixed along the axis of a cylindrical camera, the latter one having a radius of 57.2 mm. The wire could be heated by means of an electric current of known intensity, its temperature at every moment being checked by means of a calibrated HOLBORN-KURLBAUM-pyrometer. The film was wrapped in black paper and applied to the outside of the camera; the increase of the radius by this sheet of paper was 0.15 mm. As rhodium above 600° C. is readily attacked by oxygen, the camera was surrounded by a cylindrical brass box, which during the experiments was continuously evacuated. The wire was heated at 750°, 1200° and 1400° C. successively and originally kept in an immovable position. Later-on the experiments were repeated with

<sup>1)</sup> A. W. HULL and W. P. DAVEY, Phys. Review, **17**, (1921), 571. Their value for  $a_0$  was 3.820 Å. in the case of an electrolytically deposited rhodium. T. BARTH and G. LUNDE. Zeits. f. phys. Chem., **117**, (1925), 478, found  $a_0 = 3.795$  Å. for the metal prepared by reduction of the oxide. A remarkable fact is, that for a wire previously heated,  $a_0$  usually varies between 3.77 and 3.80 Å.

<sup>2)</sup> Before drawing the wire, the metal had previously been heated at 900°—1000° C

TABLE II.  
Rhodium-Wire, drawn; diameter: 0.3 mm. At Ordinary Temperature.

N <sup>o</sup> . of Lines	2l in mm.:	Int.:	$\lambda$ :	$\theta$ :	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	Indices {h k l}:
1	68.34	1	$\alpha$	17° 4'	0.0861	0.0825	(110)*
2	74.27	2	$\beta$	18 33	0.1012	0.1005	(111)
3	82.80	7	$\alpha$	20 41	0.1247	0.1237	(111)
4	86.28	3	$\beta$	21 33	0.1349	0.1340	(200)
5	96.09	7	$\alpha$	24 0	0.1654	0.1649	(200)
6	109.01	2	$\alpha$	27 13	0.2093	0.2061	(210)*
7	125.12	3	$\beta$	31 15	0.2691	0.2679	(220)
8	140.65	9	$\alpha$	35 8	0.3312	0.3298	(220)
9	150.30	3	$\beta$	37 52	0.3711	0.3684	(311)
10	159.23	1	$\beta$	39 46	0.4092	0.4019	(222)
11	169.92	9	$\alpha$	42 26	0.4552	0.4535	(311)
12	179.29	4	$\alpha$	44 47	0.4962	0.4948	(222)
13	187.46	1	$\beta$	46 49	0.5316	0.5358	(400)
14	212.60	2	$\beta$	53 6	0.6395	0.6363	(331)
15	217.61	3+	$\alpha$	54 21	0.6603	0.6596	(400)
16	220.69	2	$\beta$	55 7	0.6729	0.6698	(420)
17	249.35 ( $\Delta$ )	7	$\alpha$	62 17	0.7831	0.7834	(331)
18	255.96	2	$\beta$	63 56	0.8069	0.8038	(422)
19	261.25 ( $\Delta$ )	7	$\alpha$	65 15	0.8247	0.8246	(420)
20	290.27	3	$\alpha$	72 30	0.9095	0.9071	(332)*

Radius of Camera: 57.35 mm. Exposure: 20—40 m. Amp. hours.

Radiation: Copper-anticathode;  $\lambda_{\alpha} = 1.540 \text{ \AA}$ ;  $\lambda_{\beta} = 1.388 \text{ \AA}$ .

The values here given are the mean values of three series of measurements; the distances 2l were measured on the Comparator.  $\Delta$  are doublets.

Quadratic Equation: for the  $\alpha$ -radiation:  $\sin^2 \theta = 0.04123 \cdot (h^2 + k^2 + l^2)$ .

for the  $\beta$ -radiation:  $\sin^2 \theta = 0.03349 \cdot (h^2 + k^2 + l^2)$ .

Face-centred cubic lattice<sup>1</sup>), with  $a_0 = 3.791 \text{ \AA}$ ; from the doublets  $\Delta$  another value:  $a'_0 = 3.78 \text{ \AA}$ . can be calculated. The values marked with an \*, belong to the  $\alpha$ -modification and correspond to: (222),  $\alpha$  (521), etc. of its spectrogram.

a wire rotating about its axis with speeds varying from 60 to 5 times an hour; the apparatus used in the latter case is described below.

In the experiments with an immovable wire it was observed, that by

heating, a process of recrystallisation sets in, the composing crystallites evidently being gradually enlarged: black spots appear, first in the diffraction-lines themselves<sup>1)</sup>, which thus seem at last to have been broken up into spots of greater or smaller intensity; but soon an ever increasing number of irregularly shaped spots becomes visible, covering the whole extension of the film. When the temperature increases, the diffraction-lines gradually become fainter and fainter, the spots, however, more and more numerous. They are dispersed at random over the film; and above 1400° C. the lines at last vanish entirely, while only the spots remain.

Evidently, the large number of small crystallites in the wire, orientated in all possible directions in space, gradually are replaced by a considerably smaller number of much larger crystallites, which most probably simultaneously are orientated in some regular way with respect to the length-direction of the wire. According to POLANYI, this effect is produced because of the fact, that in the large crystallites, by their unfavorable orientation, the monochromatic radiation does not yield any longer the corresponding diffraction-lines, but the accompanying slight "white" radiation of the tube now produces a great number of superimposed LAUE-effects. By the rotation of the wire about its axis, the LAUE-effects are changed into a more or less continuous background on the film, on which the now again produced monochromatic diffraction-lines are clearly visible.

The most remarkable fact, however, is, that already at 750° C. and higher, first the outer lines, then also the other ones, are split into *two* lines, thus forming doublets which consist of an intensive line and a fainter satellite; the latter one will in the following be designed by *s*. With increasing temperature, the distance between the two components of each doublet increases, because the two components, as a consequence of the thermal dilatation of the lattice, both move towards the centre of the film, but the most intensive component apparently much more rapidly than the fainter satellite. In this way their mutual distance gradually increases. Both sets of lines exactly correspond to *two* face-centred cubic lattices which differ in their values of  $a_0$  and apparently in their coefficients of thermal expansion. The dilatations of both lattices, as calculated from the values of  $a_0$ , are graphically represented in Fig. 1. The phenomenon makes the impression, as if already at ordinary temperature, the most intensive, diffraction-lines had been unresolvable doublets, the components of which are at increasing temperatures ever more separated. This behaviour manifests itself also in the case of *palladium* and *platinum*, where *no* allotropic modifications are found; the fact, therefore, appears not to be connected with an occasional presence of an allotropic modification as the one formerly described.

By controlling experiments we have convinced ourselves, that the

<sup>1)</sup> The sharply limited spots may be expected where the crystallites already almost completely have reached their paratropic orientation; conf. A. E. VAN ARKEL, *Physica*, **3**, (1923), 84.

phenomenon described cannot be attributed to some disturbance caused by the experimental arrangement used. The divergency of the incident beam

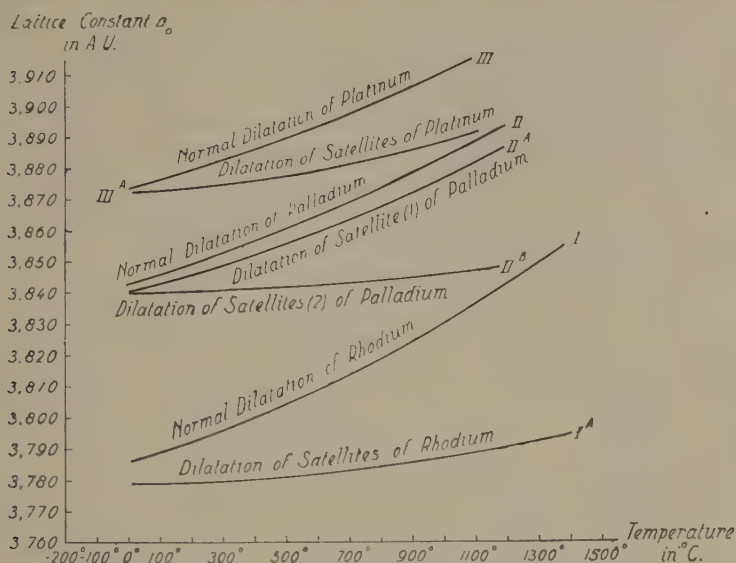


Fig. 1.

was determined to be  $1^{\circ}24'$  (conical angle  $2\psi = 2^{\circ}48'$ ). Its cross section on the wire (length 28 mm) was directly measured and found to be somewhat less than 5.4 mm. By pyrometrical measurements the length of the heated wire in the centre of the camera, which glowed at a practically uniform temperature, was found to be: at  $800^{\circ}\text{C}$ ., 7 to 8 mm; at  $1000^{\circ}\text{C}$ ., 14 mm; at  $1200^{\circ}\text{C}$ ., 15 mm. At the top and at the bottom of the film, the temperature of the wire was about  $20^{\circ}$  lower than in the centre. From these data it can be concluded, that the pencil of incident X-rays covered the full middle part of the glowing wire over a length, which entirely was situated within the field of uniform temperature, its extension being, especially at the higher temperatures, considerably greater than the part intercepted by the weakly divergent beam. No source of error can, therefore, be produced by the colder extremities of the wire. In the experiments later to be described, we carefully have studied, what influence a possibly occurring stress in the wire might have produced, be it by incomplete thermal dilatation or by the pull of a small weight fixed at the lower end of the wire; or whether perhaps a torsion produced in the wire during its rotation, might be considered as the cause of the phenomenon described. It appeared, however, that the doublets are produced in the same way as before, if all these sources of possible disturbances are beforehand eliminated. Neither does heating with direct or with alternating current alter the phenomena described, save for a little broadening of all lines.



The phenomenon must therefore be considered as a *real* one, it being only dependant on the temperature of the wire.

§ 5. As we shall have much to do with these doublets, in the following, it is advisable here already, to ask ourselves, whether this curious phenomenon of the splitting of the diffraction-lines in the spectrograms possibly has anything to do with absorption-phenomena occurring in the wire?

Now, there are three cases to be discerned<sup>1)</sup>: either the absorption of the *X*-rays in the material investigated is complete; or there is no

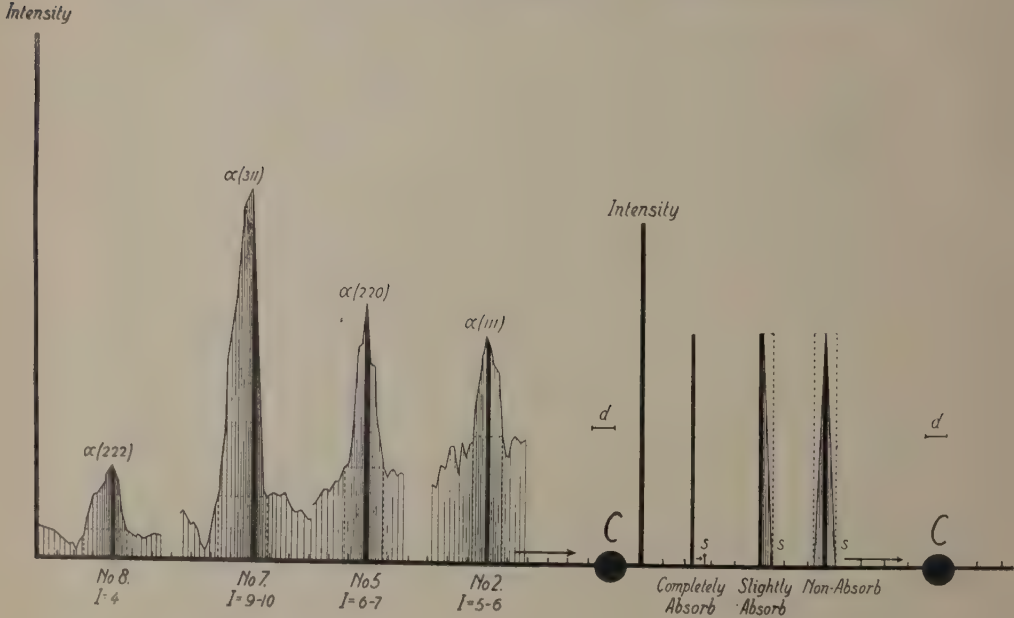


Fig. 2. Intensity-distribution within the Diffraction-lines.

absorption at all; or the rays are partially absorbed, — which in practice is the most ordinary case.

If a substance completely absorbs the incident *X*-rays, then the lines exclusively are generated by diffraction at structural planes situated at the surface of the wire. A thin, sharply limited line will be produced in this case, the position of which will only be shifted through a little distance, depending on the diameter *d* of the exposed wire and on the glancing angle  $\theta$ . If the substance only partially absorbs the incident rays, the line will have its maximum intensity at the side most distant from the centre of

<sup>1)</sup> A. HADDING, *Centr. Blatt Miner.*, (1921), 631. See for the corrections to be applied also: P. DEBIJE, *Phys. Zeits.*, **18**, (1917), 5; W. GERLACH and O. PAULI, *Zeits. f. Phys.*, **7**, (1921), 116; A. J. BIJL and N. H. KOLKMEIJER, *Proceed. R. Acad. Amsterdam*, **21**, (19), 496; F. G. FOOTE, F. C. BLAKE and W. G. FRANCE, *Journ. of phys. Chem.*, **34**, (1930) 2236.

the film; the intensity within the line itself gradually falling off towards the centre of the spectrogram; while, if the substance does not at all absorb, the lines will be most intensive in the middle part of their extension, the intensity gradually diminishing in a symmetrical way towards the borders of the line.

We, therefore, have studied the intensity-distribution within the borders of the lines themselves, by means of photometrical measurements, using a thermopile and a sensitive galvanometer. The result was, that the lines near the centre of the film were almost symmetrically built; which proved, that only little absorption in the thin wire takes place. The lines more distant from the centre, however, showed a distinctly *unsymmetrical* distribution of their intensity; but, here the most intensive part appeared always to be turned *towards the centre of the film*, i.e. exactly the reverse of what should be expected in the case of the absorption-phenomena mentioned above; the intensity slowly falls off towards the outwardly placed satellite. There can, therefore, be no doubt as to the quite different character of the origin of the observed lines.

§ 6. For the purpose of a more detailed study of these phenomena, we have made use of a camera<sup>1)</sup> allowing the rotation of a heated wire within a perfect vacuum.

The camera consists of a cylindrical brass box  $KK'$ , with a diameter of

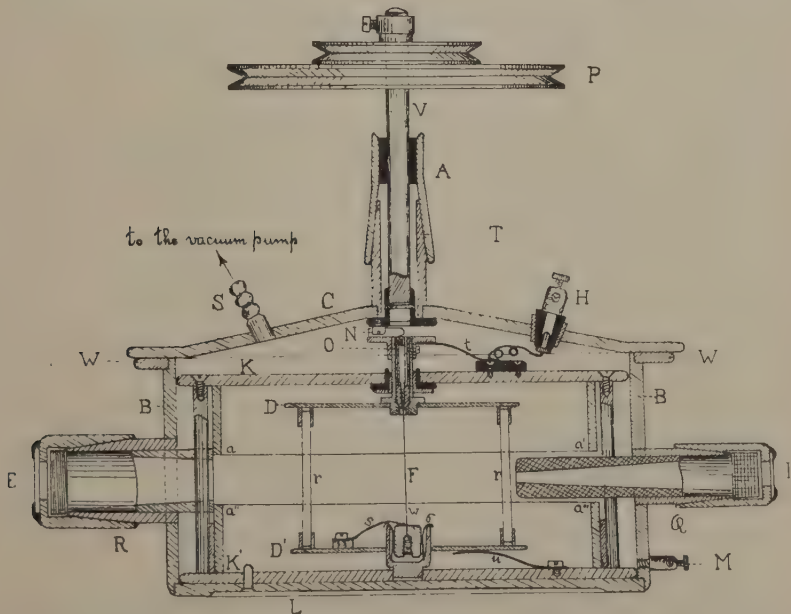


Fig. 3.

<sup>1)</sup> This instrument was built in the shop of the laboratory by the mechanics A. VAN DER MEULEN and J. OLYSLAGERS.

114.4 mm. The central part of its vertical wall is cut, so that a horizontal slit is formed of about 2 cm broadness; the  $X$ -rays passing this opening  $aa'a''a'''$ , can reach the photographic film, which is fixed at the outside of the camera by means of two excentric handles, which uniformly press it against the outer wall of the camera.  $BLB'$  is the wall of the vacuum chamber, equally made of brass and completely surrounding the camera  $KK'$ . Its lid  $C$ , provided with a broad, flattened and smoothly polished brim  $W$ , rests on the similar flat and carefully polished brim of the wall  $BB'$ , — the locking thus obtained being perfectly air-tight, if the brims are greased. The outlet  $S$  is connected with the vacuum-pump; on the other hand,  $H$  is the connection for the heating current (1—4 Amp.), while at the bottom of the chamber  $M$  represents the other electrode. The cover  $C$ , moreover, bears a removable projecting part, also made of brass, which has a conically shaped and carefully ground and polished surface at  $T$ , exactly fitting into an equally well polished conical tube  $A$ . This, in its turn, is immovably fixed to the axis of rotation  $V$ . This last one is moved by an electrical motor, which is provided with a transmission, consisting of an endless screw and cog-wheel, while its motion is transferred to the pulley  $P$ , by means of a string. During the rotation, the friction at the air-tight joint  $T$  is considerably reduced by thoroughly greasing the conical surfaces. The collimator  $Q$  fits in the wall of the vacuum-chamber, and is provided with the usual leaden screens and slits. The pencil of  $X$ -rays enters the chamber at  $I$  and leaves it at  $E$  through a very thin glass window, which simultaneously allows of observing the glowing wire and of controlling its temperature at each moment by means of a calibrated optical pyrometer.

The axis of rotation  $A$ , at its lower end, bears a cog  $N$ , which, by the revolution of  $A$ , drags along the equally smoothly rotating part  $O$ , to which at the inside of the camera  $KK'$  the circular supports  $D$  and  $D'$  are fastened, joined together by three thin glass rods  $r$ . Within this light, movable framework  $DrD'r$ , the metallic and heated wire  $F$  to be studied is centrically fixed, its lower end bearing a small, carefully polished brass weight  $W$ . This last one is freely movable between the extremely flabby, very soft springs  $\sigma$ , which during its motion are perfectly gliding along it, steadily remaining in contact with it, but not causing any appreciable friction. These springs  $\sigma$  simultaneously are the contacts for the heating current, by which the wire  $F$  can be heated at different temperatures. Similarly, the springs  $t$ ,  $s$  and  $u$  also are very soft and gliding contacts; they are necessary either as places of contact for the heating current or they are applied solely with the purpose of keeping the movable framework within the camera in the desired, perfectly central position.

The motion of  $P$  was in our experiments mostly regulated, in such a way that the number of rotations ordinarily remained within the limit of sixty each hour; it could, however, be diminished at five an hour. The black coloured parts in Fig. 3 all represent insulating materials (ebonite, piceine,



TABLE III.  
Rhodium-Wire, drawn; diameter: 0.3 mm., at Different Temperatures.

No. of Line:	VI. At ordinary Temperature, fixed or rotating about its axis.				III. At 750° C.; fixed.				IV. At 1000° C.; fixed.				V. At 1400° C.; fixed.				$\lambda$ :	Indices $\{hkl\}$ :
	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):		
1	—		—	—	84.64	1+	0.1301	0.1287	—		—	—	—		—	—	$\alpha$	(110)*
2	95.00	2	0.1617	0.1615	94.79	2	0.1601	0.1582	94.03	1	0.1588	0.1569	—		—	—	$\beta$	(111)
3	—		—	—	104.89	4	0.1936	0.1930	104.15	4	0.1924	0.1914	102.32	—	0.1860	0.1877	$\alpha$	(111)
3A	105.57	7	0.1972	0.1972	—		—	—	105.46 (s)	2	0.1967	0.1961	105.16 (s)	—	0.1956	0.1952	$\alpha$	(111)
4	111.06	2	0.2165	0.2154	110.45	2	0.2133	0.2109	109.51	1	0.2111	0.2092	—		—	—	$\beta$	(200)
5	—		—	—	122.69	5	0.2585	0.2573	121.73	4	0.2558	0.2552	119.86	—	0.2490	0.2503	$\alpha$	(200)
5A	123.45	6	0.2625	0.2629	—		—	—	123.36 (s)	2	0.2622	0.2614	122.60 (s)	—	0.2594	0.2603	$\alpha$	(200)
6	—		—	—	162.84	1	0.4239	0.4218	161.91	1	0.4206	0.4184	—		—	—	$\beta$	(220)
6A	164.71	3	0.4330	0.4308	—		—	—	163.57 (s)	1	0.4310	0.4289	—		—	—	$\beta$	(220)
7	—		—	—	183.86	5	0.5163	0.5146	182.45	4	0.5100	0.5104	181.06	—	0.5038	0.5006	$\alpha$	(220)
7A	185.80	7	0.5245	0.5258	185.59 (s)	2	0.5228	0.5235	185.22 (s)	2	0.5218	0.5228	184.92 (s)	—	0.5207	0.5206	$\alpha$	(220)
8	—		—	—	199.25	2-	0.5821	0.5801	197.62	2	0.5765	0.5753	—		—	—	$\beta$	(311)
8A	201.68	2+	0.5931	0.5923	200.97 (s)	1	0.5891	0.5909	200.92 (s)	1	0.5897	0.5895	—		—	—	$\beta$	(311)
9	214.37	1	0.6467	0.6461	213.28	1	0.6422	0.6433	—		—	—	—		—	—	$\beta$	(222)
10	—		—	—	229.50	8	0.7091	0.7076	227.27	8	0.6993	0.7019	225.46	—	0.6922	0.6884	$\alpha$	(311)
10A	232.50	9	0.7203	0.7229	232.24 (s)	4+	0.7185	0.7198	231.94 (s)	5	0.7179	0.7190	—		—	—	$\alpha$	(311)
11	—		—	—	246.71	4+	0.7734	0.7720	243.62	5	0.7627	0.7657	241.04	—	0.7530	0.7510	$\alpha$	(222)
11A	249.87	4	0.7854	0.7886	249.67 (s)	2	0.7840	0.7851	248.60 (s)	2	0.7808	0.7843	—		—	—	$\alpha$	(222)
12	272.51	1	0.8603	0.8616	—		—	—	—		—	—	—		—	—	$\beta$	(400)

Radius of Camera: 57.35 mm. (corr.). All distances 2l are measured on the Comparator.

Radiation: Iron-anticathode;  $\lambda_{\alpha} = 1.9366 \text{ \AA}$ ,  $\lambda_{\beta} = 1.753 \text{ \AA}$ .

Quadratic Equations: for  $\alpha$ -radiation,  $\sin^2 \theta = A \cdot (h^2 + k^2 + l^2)$ . } The coefficients A and B, and the corresponding parameters  $a_0$ , are given below for each  
for  $\beta$ -radiation,  $\sin^2 \theta = B \cdot (h^2 + k^2 + l^2)$ . } case separately.

With (s) are indicated the satellites of the stronger lines of each doublet, generated on heating the fixed wire; with Int. the visually estimated intensities.

$A = 0.06572$ .  
 $B = 0.05385$ .  
 $a_0 = 3.777 \text{ \AA}$ .

$A = 0.06433$ .  
 $B = 0.05273$ .  
 $a_0 = 3.817 \text{ \AA}$ .

$A = 0.06381$ .  
 $B = 0.05230$ .  
 $a_0 = 3.832 \text{ \AA}$ .

$A = 0.06258$ .  
 $B = 0.05130$ .  
 $a_0 = 3.870 \text{ \AA}$ .

$A'_s = 0.06548$ .  
 $B'_s = 0.05367$ .  
 $a'_0 = 3.784 \text{ \AA}$ .

$A'_s = 0.06536$ .  
 $B'_s = 0.05359$ .  
 $a'_0 = 3.787 \text{ \AA}$ .

$A'_s = 0.06502$ .  
 $B'_s = 0.05330$ .  
 $a'_0 = 3.796 \text{ \AA}$ .

In all three cases, the exposure was: 80 m.Amp. hours.

Exposure: 60 m.Am. hours. The spectrograms of the fixed and of the rotated wire were identical, their lines corresponding in both cases to the satellites, developed on heating.

Moreover, the line indicated with \* corresponds to the  $\alpha$ -modification:  $\alpha$  (222).

The other lines also seem to be doublets; but the spectrogram was too faint for allowing their measurement. For the same reason no estimation of the intensities were made in this case.



etc.). The apparatus has, up till now, completely answered its purpose, even at temperatures as high as  $1600^{\circ}\text{C}$ . By repeatedly heating in a vacuum at high temperatures, all gases occluded in the wire were finally driven out. Most experiments were made with a wire previously used in the measurements of the thermoelectric force, it thus being heated for a long time at temperatures as high as  $1600^{\circ}\text{C}$ . The surface of the wire appeared under the microscope to be rather smooth and it was *not* altered, even after repeatedly heating it. Occasional inequalities in this respect were, moreover, counterbalanced by rotating the wire during the experiments about its axis.

§ 7. By means of this arrangement it now is possible to study the heated wires as well, when they are immovable, as when they are rotated about their axis. The phenomena observed in both cases are the following.

A. If a wire is heated at  $1500^{\circ}\text{C}$ ., finally all lines disappear and only innumeral spots remain visible, distributed at random over the film; when again cooled down to ordinary temperature, such a wire, if radiated through, only yields spots <sup>1)</sup>. But if this cooled wire now be rotated about its axis, all lines on the film reappear at their exact places, *they all coinciding this time with the positions of the former satellites of each doublet*. As rhodium is a very plastic metal, possessing many gliding planes, evidently the crystallites, enlarged by recrystallisation, for the greater part gradually become arranged parallel to each other, — probably, as ETTISCH, POLANYI and WEISSENBERG <sup>2)</sup> have demonstrated, with [111] and [100] as paratropic directions, parallel to the length-direction of the wire. The significance of the spots and their vanishing on rotating the wire have already been explained in the above.

B. If the wire be heated at  $900^{\circ}\text{C}$ . and simultaneously rotated about its axis, a normal spectrogram of intensive lines appears; but this time *all lines coincide with the positions of the former intensive lines* of the doublets and *not* with those of the satellites; the latter ones, for the greater part, seem to have completely disappeared <sup>3)</sup>. From the following data, this peculiar behaviour at once becomes evident:

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<sup>1)</sup> Such a wire was preserved during 9 weeks. After this lapse of time, the wire was, in an immovable position, again studied with iron-radiation at  $20^{\circ}\text{C}$ . Now the beginnings of regular diffraction-lines really appeared in the spectrogram, but still amongst a great number of spots. Evidently during these 9 weeks the inner structure of the wire had already changed, the larger crystallites gradually either having crumbled down to smaller ones or partially having lost their paratropic orientation. These experiments will after some months once more be repeated.

<sup>2)</sup> M. ETTISCH, M. POLANYI and K. WEISSENBERG, *Zeits. f. Physik*, 7, (1921), 181.

<sup>3)</sup> This vanishing of the satellites must not be taken too literally, as it simply is a question of intensities. Indeed, in the case of *palladium* and *platinum* we occasionally obtained spectrograms, in which, — even after rotation; — a number of satellites remained visible. In judging the position of the lines, the small shift must of course be taken into account, which is a consequence of the thermal dilatation of the lattice at higher temperatures; but this fact does not lead to any confusion, if the comparison be carefully made.



I Rotating wire at 20° C. 2 l in mM.:	II Immovable wire at 750° C. 2 l in mM.:	III Rotating wire at 900° C. 2 l in mM.:	IV Immovable wire at 1000° C. 2 l in mM.:
95.0	94.79	94.24	94.03
105.57	104.89		$\Delta \left\{ \begin{array}{l} 104.15 \\ 105.46 \end{array} \right. (S)$
111.0	110.45	109.48	109.51
123.45	122.69	122.10	$\Delta \left\{ \begin{array}{l} 121.73 \\ 123.36 \end{array} \right. (S)$
164.7	162.84	162.12	$\Delta \left\{ \begin{array}{l} 161.91 \\ 163.57 \end{array} \right. (S)$
185.50	$\Delta \left\{ \begin{array}{l} 183.86 \\ 185.59 \end{array} \right. (S)$	182.97	$\Delta \left\{ \begin{array}{l} 183.45 \\ 185.22 \end{array} \right. (S)$
201.86	$\Delta \left\{ \begin{array}{l} 199.25 \\ 200.97 \end{array} \right. (S)$	198.44	$\Delta \left\{ \begin{array}{l} 197.62 \\ 200.92 \end{array} \right. (S)$
232.50	$\Delta \left\{ \begin{array}{l} 229.50 \\ 232.24 \end{array} \right. (S)$	228.0	$\Delta \left\{ \begin{array}{l} 227.27 \\ 231.94 \end{array} \right. (S)$
249.87	$\Delta \left\{ \begin{array}{l} 246.71 \\ 249.67 \end{array} \right. (S)$	244.40	$\Delta \left\{ \begin{array}{l} 243.62 \\ 248.60 \end{array} \right. (S)$

The phenomena observed at different temperatures may, moreover, be seen from Table III, in which the values of  $2l$ , of  $\sin^2 \theta$  and the indices  $\{hkl\}$  for *rhodium* under different conditions are collected, as well the coefficients  $A$  and  $B$ , as the parameters  $a_0$  for each of the apparently occurring face-centred lattices being calculated in each case.

Four spectrograms were obtained at 800° C. with *the same* wire and the same camera, but the heating and exposure were consecutively extended during 6, 14, 21, and again 28 hours, alternately direct and alternating current being used in heating the wire. It appeared that *the ratio of the relative intensities of the components of each doublet was shifted towards an ever increasing intensity of the satellites in comparison with that of the other line, if the duration of the heating was augmented.* As the time-factor, therefore, appears to be of great influence, as far as the absolute intensities of the satellites be considered, there can be no doubt, that the effect observed must in some way directly be connected with the internal structure of the wire, the latter evidently being gradually changed, if the heating be continued during an ever longer interval of time.

#### § 8. *Palladium.*

The phenomena observed in the case of *palladium*, — which does not

TABLE IV.  
Palladium-Wire, drawn; diameter: 0.3 mm., at Different Temperatures.

No. of Line	I.A At Ordinary Temperature. (Wire immovable).				I.B At Ordinary Temperature. (Wire rotated).				II.A At 800° C. (Wire immovable).				II.B At 800° C. (Wire rotated).				III. At 1200° C. (Wire immovable).				$\lambda$ :	Indices $\{hkl\}$ :
	2l in mm.	Int.	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.	Int.	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.	Int.	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.	Int.	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.	Int.	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):		
1	93.70	3	0.1577	0.1563	93.33	2	0.1558	0.1556	93.12	2	0.1566	0.1535	92.51	3	0.1539	0.1528	92.23	2	0.1529	0.1527	$\beta$	(111)
2	103.82	7	0.1913	0.1907	103.71	6	0.1908	0.1899	103.51	5	0.1901	0.1873	102.61	7	0.1869	0.1864	102.73	5	0.1874	0.1863	$\alpha$	(111)
3	109.29	2	0.2103	0.2084	108.80	3	0.2085	0.2075	108.46	2	0.2073	0.2047	108.05	3	0.2056	0.2037	107.61	2	0.2043	0.2036	$\beta$	(200)
4	121.37	5	0.2548	0.2543	121.11	5	0.2538	0.2532	120.68	6	0.2520	0.2498	120.11	7	0.2500	0.2485	119.92	4	0.2492	0.2484	$\alpha$	(200)
4A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	121.51 (s)	1	0.2553	0.2532	$\alpha$	(200)
5	161.19	3	0.4177	0.4169	160.68	3	0.4155	0.4150	159.74	2	0.4112	0.4094	159.23	3	0.4092	0.4074	158.62	1	0.4066	0.4072	$\beta$	(220)
5A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	161.71 (s)	1	0.4198	0.4153	$\beta$	(220)
6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	176.81 (s')	2	0.4852	0.4854	$\alpha$	(220)
7	81.68	9	0.5067	0.5086	181.16	9	0.5041	0.5064	180.21	6+	0.5000	0.4995	179.31	8	0.4962	0.4970	178.64	5	0.4933	0.4968	$\alpha$	(220)
8	—	—	—	—	—	—	—	—	182.53 (s)	1	0.5102	0.5065	181.12 (s)	2	0.5041	0.5074	182.01 (s)	1	0.5078	0.5065	$\alpha$	(220)
9	—	—	—	—	—	—	—	—	194.95	2	0.5641	0.5629	193.84	3	0.5592	0.5601	193.62	1+	0.5583	0.5599	$\beta$	(311)
7A	196.46	2	0.5708	0.5732	196.32	3	0.5702	0.5706	—	—	—	—	197.41 (s)	1	0.5748	0.5720	196.51 (s)	1	0.5710	0.5708	$\beta$	(311)
10	—	—	—	—	208.57	1	0.6224	0.6224	206.35	1	0.6127	0.6140	205.64	2	0.6099	0.6110	—	—	—	—	$\beta$	(222)
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	219.31 (s)	3	0.6675	0.6674	$\alpha$	(311)
12	225.58	10	0.6927	0.6993	225.29	10	0.6916	0.6962	223.33	8	0.6835	0.6868	221.92	10	0.6778	0.6834	222.14	5	0.6787	0.6832	$\alpha$	(311)
13	—	—	—	—	—	—	—	—	226.61 (s)	2	0.6967	0.6964	225.21 (s)	2	0.6914	0.6977	225.11 (s)	1	0.6911	0.6964	$\alpha$	(311)
10A	241.70	4	0.7555	0.7628	241.30	4	0.7540	0.7595	238.11	3	0.7419	0.7492	237.43	5	0.7393	0.7456	236.42	2	0.7353	0.7453	$\alpha$	(222)
11A	—	—	—	—	—	—	—	—	242.21 (s)	1	0.7573	0.7597	242.21 (s)	1	0.7576	0.7652	239.62 (s)	1	0.7477	0.7597	$\alpha$	(222)
11	—	—	—	—	260.73	1	0.8230	0.8299	257.22 (s)	1	0.8111	0.8187	256.81	3	0.8097	0.8147	—	—	—	—	$\beta$	(400)
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	262.73	1+	0.8295	0.8145	$\beta$	(400)
12A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	263.81 (s)	1	0.8333	0.8302	$\beta$	(400)
13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	303.24	2	0.9393	0.9447	$\beta$	(331)
13A	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	309.26	2	0.9512	0.9671	$\beta$	(331)
14B	—	—	—	—	—	—	—	—	—	—	—	—	321.42	3	0.9715	0.9675	—	—	—	—	$\beta$	(331)
14	324.6	2	0.9767	0.9900	—	—	—	—	324.94	2	0.9766	0.9722	322.65	2	0.9767	0.9880	322.04	2	0.9724	0.9859	$\beta$	(331)
14A	—	—	—	—	—	—	—	—	329.13 (s)	2	0.9815	0.9859	—	—	—	—	—	—	—	—	$\beta$	(331)
15	—	—	—	—	—	—	—	—	347.52	5	0.9966	0.9989	347.63	5	0.9964	0.9941	—	—	—	—	$\alpha$	(400)

Radius of Camera: 57.35 mm. All distances 2l were measured on the Comparator.

Radiation: Iron-anticathode:  $\lambda_\alpha = 1.9366 \text{ \AA.}$ ;  $\lambda_\beta = 1.753 \text{ \AA.}$  Exposure: 60—96 m. Amp. hours.

With (s) and (s') the components of the doublets and triplets are indicated, developed on heating. Int. are the visually estimated intensities.

The lines 13—15 only can approximately be measured, because they are situated at the very borders of the film and thus appear much distorted.

$A = 0.06343.$ $B = 0.05199.$ $a_0 = 3.844 \text{ \AA.}$	$A = 0.06343.$ $B = 0.05199.$ $a_0 = 3.844 \text{ \AA.}$	$A = 0.06243.$ $B = 0.05117.$ $a_0 = 3.875 \text{ \AA.}$ $A' = 0.06331.$ $B' = 0.05189.$ $a'_0 = 3.848 \text{ \AA.}$	$A = 0.06213.$ $B = 0.05092.$ $a_0 = 3.885 \text{ \AA.}$ $A' = 0.06343.$ $B' = 0.05200.$ $a'_0 = 3.845 \text{ \AA.}$	$A = 0.06211.$ $B = 0.05090.$ $a_0 = 3.885 \text{ \AA.}$ $A' = 0.06331.$ $B' = 0.05189.$ $a'_0 = 3.848 \text{ \AA.}$	$A'' = 0.06067.$ $B'' = 0.04972.$ $a''_0 = 3.93 \text{ \AA.}$
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show any allotropic modifications and whose curve of the electrical resistance in its dependance on the temperature is a quite normal one, — are actually the same as those observed in the case of *rhodium*. But here the further complication occurs, that in the spectrogram at  $1200^{\circ}$  C. not only doublets, but also a number of *triplets* occur, the components here being indicated by  $s'$  and  $s$ ; the central lines of the triplets are always the most intensive ones of the three. The data obtained are collected in Table IV. It must be remarked that in the case of the triplets, the coincidence of the lines produced in the case of rotation of the wire, be it with the satellites or with the other ones, is not in all cases as perfect, as it is in the case of *rhodium*; in most cases all three lines remain visible.

### § 9. *Platinum*.

Also *platinum*-wires show similar phenomena, when heated in a vacuum. Some results obtained at ordinary temperature and at  $800^{\circ}$  C. are reproduced in Table V. No triplets were observed here.

§ 10. The question now arises: how to explain these facts? Neither exhausting the camera, nor filling it with a gas, like air; nor any other modification in the way of experimenting, so as to avoid any possible stress in the wire, — appeared to alter the results mentioned before to any appreciable degree.

If from the best data available in literature about the thermal dilatation of these metals (HOLBORN and DAY for *platinum* and *palladium*; FIZEAU, VALENTINER and WALLOT for *rhodium*), we calculate the values for  $a_0$  in the case of these metals, we find the following results:

*Pt* at  $800^{\circ}$  C.:  $a_0 = 3.908 \text{ \AA}$ ; *Pd* at  $800^{\circ}$  C.:  $a_0 = 3.885 \text{ \AA}$ ; at  $1000^{\circ}$  C.:  $3.895 \text{ \AA}$ ; at  $1200^{\circ}$  C.:  $3.910 \text{ \AA}$ ; *Rho* at  $750^{\circ}$  C.:  $a_0 = 3.81 \text{ \AA}$ ; at  $1000^{\circ}$  C.:  $3.83 \text{ \AA}$ ; at  $1400^{\circ}$  C.:  $3.85 \text{ \AA}$ .

In comparing these values with those calculated from our direct experiments, there can be no doubt about the fact, that in each case studied the *inner* component of each doublet or triplet corresponds to that value of  $a_0$ , which results from the *normal* thermal dilatation of the lattice; the outer satellite, on the other hand, corresponds to the original value of  $a_0$  at room-temperature or a slightly higher one. In the case of the triplets, the central most intensive component corresponds to the dilatation at a temperature, somewhere between those of the two other components. These facts stamp the phenomenon observed as one of a very particular kind of "thermal hysteresis", which doubtlessly must intimately be connected as well with the process of recrystallisation going on at higher temperatures, as with the paratropic orientation of those enlarged crystallites with respect to the length-direction of the wire. There must be some reason, why a minor part of the crystallites present are impeded in their normal thermal dilatation by

TABLE V.  
Platinum-Wire, drawn; diameter: 0.3 mm.

At Ordinary Temperature.					At 800° C. (rotating wire).					
Nº. of line:	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	2l in mm.:	Int.:	$\sin^2 \theta$ (obs.):	$\sin^2 \theta$ (calc.):	$\lambda$ :	Indices $\{hkl\}$ :
1	92.73	3	0.1547	0.1536	92.03	1	0.1524	0.1501	$\beta$	(111)
2	103.11	6	0.1888	0.1874	101.82	3	0.1844	0.1840	$\alpha$	(111)
3	108.25	3	0.2067	0.2048	107.19	4	0.2029	0.2001	$\beta$	(200)
4	120.45	6+	0.2513	0.2499	119.19	8	0.2465	0.2454	$\alpha$	(200)
5	159.75	4	0.4117	0.4096	157.96	4	0.4073	0.4002	$\beta$	(220)
6	180.18	9	0.5004	0.4998	177.72	8	0.4894	0.4908	$\alpha$	(220)
6A	—	—	—	—	180.70	2+	0.5023	0.4976	$\alpha$	(220)
7	195.10	6	0.5649	0.5633	192.32	3	0.5529	0.5503	$\beta$	(311)
8	207.52	2	0.6181	0.6145	—	—	—	—	$\beta$	(222)
9	223.44	10	0.6842	0.6873	220.06	8	0.6704	0.6748	$\alpha$	(311)
9A	—	—	—	—	223.20	1	0.6832	0.6841	$\alpha$	(311)
10	238.89	7	0.7449	0.7498	235.28	2	0.7311	0.7362	$\alpha$	(222)
10A	—	—	—	—	238.35	2	0.7429	0.7464	$\alpha$	(222)
11	258.65	2	0.8162	0.8194	254.05	4	0.8002	0.8005	$\beta$	(400)

Radius of Camera: 57.35 mm.

Exposure: 80 m.Amp. hours.

Iron-radiation:  $\lambda_\alpha = 1.9366 \text{ \AA}$ ;  $\lambda_\beta = 1.753 \text{ \AA}$ . The lines are all measured on the Comparator.

The satellites also remain visible on rotating the wire.

$$A = 0.06248.$$

$$B = 0.05121.$$

$$a_0 = 3.874 \text{ \AA}.$$

Two lines more were visible at the very ends of the film; but they were not suited for accurate measurements.

$$A = 0.06135.$$

$$B = 0.05003.$$

$$a_0 = 3.909 \text{ \AA}.$$

$$A' = 0.06219.$$

$$B' = 0.05097.$$

$$a'_0 = 3.883 \text{ \AA}.$$

Here the change in the relative intensities of some lines, e.g. of 2 and 3; 4 and 6; 7, 9 and 10; 10 and 11, is remarkable. The same occurs at 1000° C.; line 3 is about twice as intensive as 5 at this temperature.

the presence of the major part of the surrounding and parallelly orientated individuals, — which, in their turn, either freely can expand (doublets), or partly can do so, while others also remain behind (triplets) at some intermediate temperature. It is a remarkable fact, that the appearance of triplets at a given temperature seems to be limited to some lines, like (220), (311),

(331), while the other lines at that same temperature only are transformed into doublets. Most remarkable, however, is, that in the spectrograms *no broad, smeared-out bands* are found, as beforehand would be expected, but *quite sharp lines*, forming doublets or triplets, although the heating of the wire in all cases has gone on during no less than 8 or 10 hours consecutively. If the duration of the heating is prolonged, the relative intensities of the satellites with respect to the other components are increased, in stead of being diminished, as one perhaps beforehand would expect.

The fact, that a wire after being kept at a temperature high enough to yield only irregularly distributed spots in the spectrogram, and after having been preserved for some months, again begins to show lines, — directly proves, that such a wire has reached a state, which at lower temperatures is an unstable one; it gradually, although extremely slowly, goes back to its original internal structure, which for a good deal consists of small crystallites arbitrarily orientated in space. The larger crystallites generated by the process of recrystallisation at higher temperatures, evidently at room-temperature partially crumble down into smaller individuals or loose their paratropic orientation. Also the other phenomenon: that such a heated wire again yields a normal spectrogram, as soon as it be rotated about its axis, — is an indication of the fact, that a more thoroughly regular orientation of the enlarged crystallites with respect to the length-direction of the wire really accompanies the process of recrystallisation at higher temperatures; which orientation, — in contrast to what has been stated by some other investigators, — evidently also partially and gradually gets lost at lower temperatures, if the wire only be preserved during a sufficiently long time. As to the orientation with respect to the length-direction of the wire, — this doubtlessly is, also in these cases, connected with the presence of gliding planes in the crystallites: *rhodium* and *palladium*, for instance, are so plastic, that even at ordinary temperature they cannot be ground in a mortar without being flattened out into thin layers. Most probably [111] and [100] are the principal paratropic directions in such wires, if drawn out at somewhat higher temperatures. The paratropic orientation of the crystallites composing the wire can, however, be no complete one, neither at ordinary, nor at higher temperatures; because on rotating the wire, constantly the lines (111), (311) and (331) occur and they belong to the most intensive ones: these diffraction-lines belong<sup>1)</sup>, however, neither to the zone [111], nor to the zone [100]. It must, therefore, be assumed that in such a drawn wire, at least a certain number of the composing crystallites preserve their arbitrary orientation in space besides the other

<sup>1)</sup> The triplets: (110), (220), (221), (331), (332) belong to a zone with the zonal axis [110]: (111), (200), (300), (311), (222), (400), (422) to a zone with the axis [011]; triplets like: (110), (220), (200), (300), (400), (310), (420), also to a zone with the axis [001]; etc. etc.



ones. Perhaps this contrast between the two groups may something have to do with the retardation in the thermal dilatation observed.

Momentaneously no final explanation of the curious phenomena observed can yet be given. The investigations are, therefore, continued, especially with the purpose of elucidating the apparently *discontinuous* character of the effect.

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**Physics.** — *Temperature determination from bandspectra. I. Vibrational energy distribution and vibrational transition probabilities in the Cyanogen  ${}^2\Sigma - {}^2\Sigma$  bandsystem.* By L. S. ORNSTEIN and H. BRINKMAN. (Communication from the Physical Institute of the University of Utrecht).

(Communicated at the meeting of January 31, 1931).

§ 1. The temperature determination from bandspectra by intensity measurements of band lines has given interesting results in several cases <sup>1)</sup>. The temperature measurements in an electric arc by ORNSTEIN and VAN WIJK have been completed by the writers. It appeared that in the centre of the arc temperatures between  $5000^\circ - 7000^\circ$  abs. exist, dependent on the current in and the length of the arc. The results of this investigation will be published in the second communication.

It is of great interest to determine the vibrational energy distribution in a bandspectrum emitted by an arc, in order to examine the distribution of the molecules among the different initial vibrational states and to control whether it agrees, just as in the case of rotational levels, with the gas temperature.

If  $p_{n'n''}$  be the transition probability from the initial vibrational state  $n'$  to the final state  $n''$ , the band intensity is, if temperature equilibrium holds:

$$I = A\nu^4 p_{n'n''} e^{-\frac{E_{n'}}{k \cdot T}} \dots \dots \dots (1)$$

( $A$  = constant,  $E_{n'}$  = initial vibrational energy,  $k$  = Boltzmann constant,  $T$  = absolute temperature,  $\nu$  = frequency).

The intensity measurements by ELLIOTT <sup>2)</sup> show that the vibrational energy distribution in the  $\beta$  bandsystem of  $BO$ , excited in active nitrogen, can not be described by a BOLTZMANN law. In the case of an electric arc, however, it appears that a distribution temperature for the vibrational levels exists, which is the same as for the rotational levels.

§ 2. The intensity distribution in the violet cyanogen bandsystem (electronic transition  ${}^2\Sigma - {}^2\Sigma$ ) has been investigated. The lightsource is a carbon arc (arc length 7 — 8 mm, current 1.7 Amp., arc voltage 105 Volt). A prism spectograph is used with a dispersion varying from 15 Å per mm at  $\lambda 3600$  Å to 36 Å per mm at  $\lambda 4600$  Å.

In the usual way the density marks are photographed with the same time of exposure as the cyanogen bands, and the plates are photometred.

- <sup>1)</sup> L. S. ORNSTEIN and W. R. v. WIJK, Z.S. f. Phys. **49**, 315, 1928.  
W. R. v. WIJK, *ibid.* **59**, 313, 1930; diss. Utrecht 1930.  
L. S. ORNSTEIN and W. R. v. WIJK, Proc. Amsterdam **33**, **44**, 1930.  
A. E. LINDH. Z.S. f. Phys. **67**, 67, 1931.  
A. ELLIOTT, *ibid.* **67**, 75, 1931.
- <sup>2)</sup> A. ELLIOTT, diss. Utrecht 1930; Z.S. f. Physik **67**, 75, 1931.

As "band intensity" we take the maximum intensity of the bandhead. The bandheads consist of many superposed lines of the *P*-branch of different wave-lengths. Thus the heads may be considered as parts of a continuous spectrum and in the intensity measurement no correction for dispersion ought to be applied. Only the variation in intensity of the standard lamp with wave-length must be taken into account.

In each sequence the bands (except the first) are disturbed by the branches of the foregoing bands of the sequence. From the maximum intensities of the heads these disturbing intensities have been subtracted.

In table I the observed intensities (divided by  $\nu^4$ ) from two plates

TABLE I.

Band $n' \rightarrow n''$	Intensity $\nu^4$ from Plate 1	Intensity $\nu^4$ from Plate 2	Mean band intensity	Surface intensity/ $\nu^4$ (grating)
0-2	3.0		3.0	
1-3	4.1		4.1	
2-4	3.2		3.2	
3-5	2.4		2.4	
4-6	2.4		2.4	
5-7	1.9		1.9	
6-8	1.3		1.3	
	Mean value of 2 spectra			
0-1	58	51	55	
1-2	61	51	57	
2-3	46	39	43	
3-4	33	27	30	
4-5	26	25	26	
5-6	20	18	19	
	5 spectra		Mean value of 4 spectra	
0-0	1000	1000	1000	1000
1-1	530	498	514	512
2-2	267	275	271	237
3-3	119	155	137	160
4-4	74	105	90	—
	3 spectra		3 spectra	
1-0	101	91	97	
2-1	104	100	102	
3-2	52	49	51	
	5 spectra		3 spectra	

are given. They are the mean values of a number of spectra, noted in the table. In the fourth column the mean  $\frac{\text{Intensity}}{\nu^4}$  from both plates is given. The accuracy reached, is different for the various sequences. The mean error may be about 10 %.

In figs. 1 and 2 for each sequence the logarithms of the bandintensities (represented by the circles) are plotted against the energy of the initial vibrational level.

In the case of  $\Delta n = 0$  we obtain a straight line; this holds also for the other sequences if we except the first measured band intensity<sup>1)</sup>. In § 3 of this article we come back on this relation.

In each sequence only a little number of band intensities could be measured; using the straight lines in figs. 1 and 2 to extrapolate the intensities of the following bands in a sequence (represented in the figs. by squares) we find that these bands are intense enough to be observed, at least in the sequences  $\Delta n = 0$  and  $-1$ . But in a given sequence the bandorigins form a „head” and run back to the long wave-length side for the higher vibrational transitions<sup>2)</sup>. Also the frequencies of the band-heads pass through a maximum. The intensity measurement of these already faint bands is only possible with a high dispersion spectrograph. The inversion of the band origins in the sequence  $\Delta n = 0$  takes place at  $n' = 5$ , while the head of band (5,5) lies between those of the bands (3,3) and (4,4). In the other sequences the bandorigins pass through a maximum at other values of  $n'$ .

But the wave-lengths of the band-heads near this maximum (for example in sequence  $\Delta n = 0$  the wavelengths of the heads (4,4), (5,5), etc.) are not exactly known; the measurement of their intensity, even with high dispersion, is not possible.

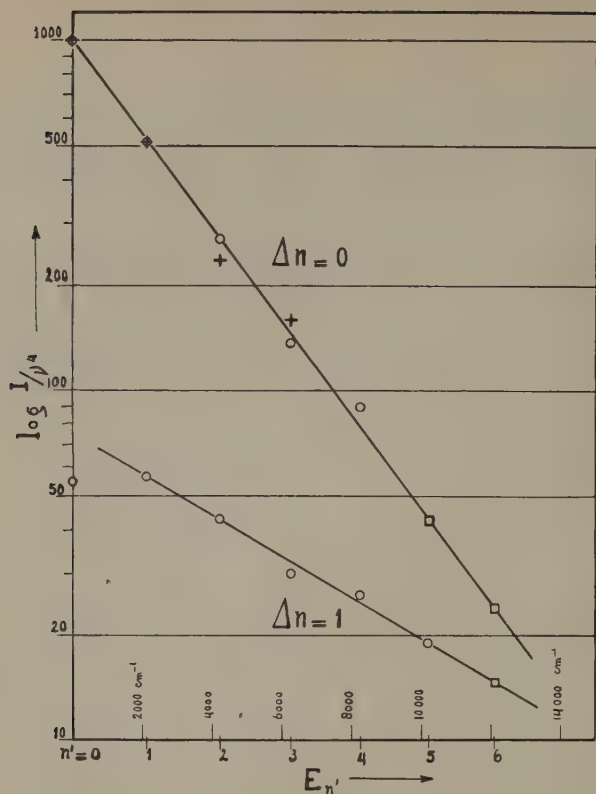
By means of a concave grating the intensity ratio of the bands (0,0), (1,1), (2,2) and (3,3), emitted by the same arc, has been checked.

The sequence  $\Delta n = 0$  is photographed in third order of the grating (dispersion about  $0.8 \text{ \AA}^{\circ}$  per mm.); by measuring the surface intensity of the bandheads we find the relative intensities (divided by  $\nu^4$ ): 1000, 512, 237, 160 (see the last column of table I; in fig. 1 these values are represented by crosses). In this measurement is taken into account that the lines of the *P*-branch forming the bandheads are different in the different bands. Measuring the maximum intensities of the heads by means of the prism spectrograph it has no reason to correct for this fact, because it is not exactly known how many *P*-lines form here the bandheads.

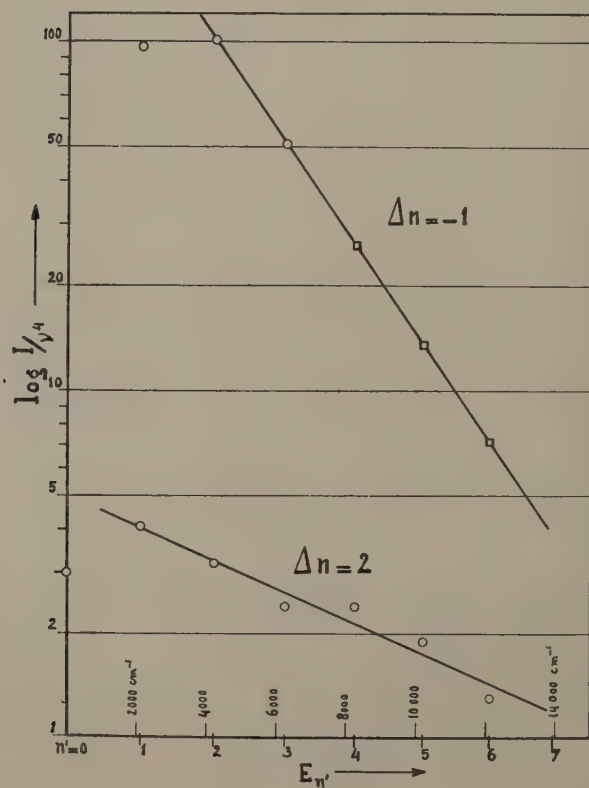
<sup>1)</sup> In the sequence  $\Delta n = -1$  we suppose that, to begin with  $n' = 2$ , also a straight line represents the relation between log. band intensity and vibrational energy in analogy with the other sequences.

<sup>2)</sup> F. A. JENKINS, Phys. Rev. **31**, 539, 1928 (see especially pag. 554).





Figs. 1 and 2. Band intensity as a function of vibrational energy. (Circles and crosses = observed intensities; squares = extrapolated intensities).



The intensities are determined from the surface of the intensity-frequency curve over a range of about  $0.8 \text{ \AA}$  (accurately known in any case) near the heads. The correction for disturbing lines of other bands could be carried out since we know the distribution temperature of the rotational levels. From the peak intensities of the undisturbed lines of band (0,0) ( $P$ -lines (2) — (8),  $P(48) - P(61)$  and  $R(1)$ ,  $R(2)$ ,  $R(4)$ ) the temperature is found to be  $6100^\circ \text{ abs.}$

The ratio of intensity from the surface and peak intensity is determined from some undisturbed lines of the band (0,0); thus the surface intensities of the lines of band (0,0) situated in the bandheads (1,1), (2,2) and (3,3) can be calculated. In the same way we determine the corrections for lines of band (1,1) falling in the heads (2,2) and (3,3), now however the intensity ratio of the bands (0,0) and (1,1) must be taken into account. In order to get this ratio we compare the same number of  $P$ -lines with the same rotation quantum numbers and find: 1000 to 512.

Proceeding in the same way for the other bands we obtain a satisfactory agreement with the measurements with the prism spectrograph (see table I and fig. 1).

In the case of the bands (0,0) and (1,1) the  $P$ -lines forming the head are exactly known. The accuracy for this intensity ratio may be 2 %.

The rotation structure of the bands (2,2) and (3,3) near the head is not analysed. By means of the bandformula of KRATZER <sup>1)</sup> we have calculated which  $P$ -lines lay in the considered wave-length region near the head <sup>2)</sup>. Since for these bands KRATZER's formula gives only an approximation of the exact frequencies of the band lines, we estimate the probable error in the relative intensities of the bands (2,2) and (3,3) at about 10 %.

By means of the straight lines in figs. 1 and 2 we extrapolate the intensities of the bands (5,5), (6,6), (6,7), (4,3), (5,4) and (6,5) <sup>3)</sup> (represented by squares in the figs. 1 and 2; underlined in table II) and obtain table II for the band intensities.

Applying the summation rule of the atomic spectra we sum up the band intensities with the same initial vibrational state. We consider these  $\sum_{n''} I'_{n''}$  for each  $n'$  as a function of the vibrational energy.

<sup>1)</sup> See for example: W. JEVONS, Proc. Roy. Soc. London **112**, 407, 1926.

<sup>2)</sup> HEURLINGER's bandformula for band (2,2) does not give the same result as KRATZER's formula. Using the former data we obtain for the relative intensity of band (2,2) 217 (instead of 237).

<sup>3)</sup> The extrapolation of the band intensities in sequence  $\Delta n = -1$  is based upon the observed intensities of the bands (2,1) and (3,2). In this sequence the frequencies of the bandorigins have a maximum at  $n'=4$ , and also the measured bandheads are situated very near together. Thus the extrapolation is uncertain.

TABLE II  
Band intensities in the Cyanogen  $2\Sigma - 2\Sigma$  band system

$n' \backslash n''$	0	1	2	3	4	5	6	7	8	$\sum_{n''} \frac{I}{\nu^4}$
0	1000	55	3							1058
1	97	514	57	4.1						672
2		102	271	43	3.2					419
3			51	137	30	2.4				220
4				<u>26</u>	90	26	2.4			144
5					<u>13</u>	<u>43</u>	19	1.9		77
6						<u>7</u>	<u>24</u>	<u>15</u>	1.3	47

The sum of the band intensities (see equation (1)), divided by  $\nu^4$ , in each  $n''$  progression may be represented by:

$$\sum_{n''} \frac{I}{\nu^4} = A \cdot e^{-\frac{E_{n'}}{kT}} (p_{n'0} + p_{n'1} + p_{n'2} + \dots) \dots \dots (2)$$

Assuming that the sum of the transition probabilities  $\sum_{n''} p_{n'n''}$  will not be very different for the different  $n''$  progressions, the sum of the band intensities  $\sum_{n''} \frac{I}{\nu^4}$  is proportional to the BOLTZMANN factor for the vibrational levels.

In fig. 3 is plotted  $\log \sum_{n''} \frac{I}{\nu^4}$  against the energy of the vibrational states  $n'$ , and we obtain a straight line, corresponding with the distribution temperature  $5500^\circ$  abs.<sup>1)</sup>, in agreement with the distribution temperature for the rotational levels:  $6100^\circ$  abs. If we do not consider the points at  $n'=5$  and  $n'=6$ , being the most uncertain, we find:  $5870^\circ$  abs. Within the limits of accuracy the distribution temperature for the vibrational and the rotational levels is the same.

§ 3. By means of equation (1) for the band intensity we can calculate the relative transition probabilities  $p_{n'n''}$ . In each sequence the logarithm of the band intensity (divided by  $\nu^4$ ) is proportional to the energy  $E_{n'}$

<sup>1)</sup> The slopes of the lines are determined with the method of the least squares.

(with the exception of the first band intensity in the sequences  $\Delta n = -1$ , 1 and 2).

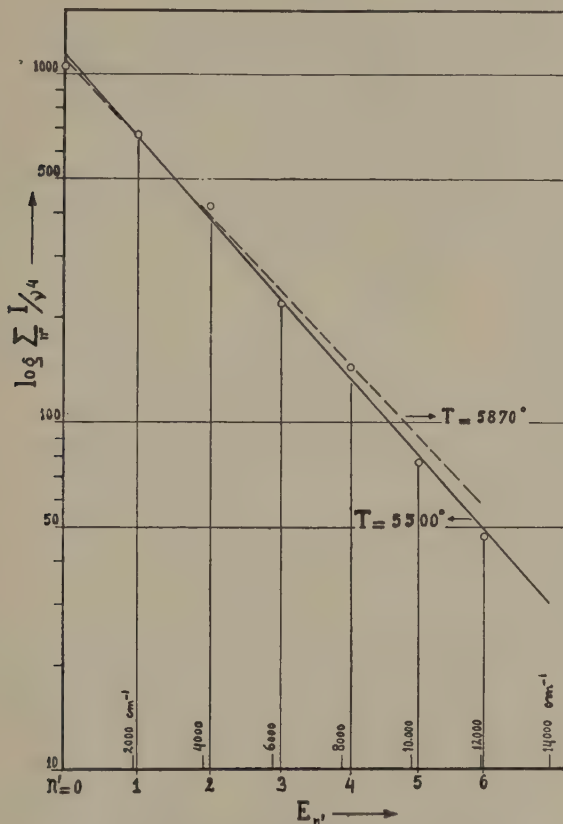


Fig. 3. The sum of the band intensities in each  $n''$  progression as a function of the vibrational energy.

Consequently the vibrational transition probabilities in each sequence are proportional to  $e^{-\alpha \cdot E_{n'}}$ , after certain value of  $n'$  ( $\alpha$  may be a constant, dependent on  $\Delta n$ ).

In the sequence  $\Delta n = 0$  this holds for all values of  $n'$ , and here is  $\alpha > 0$ . In the case of  $\Delta n = 1$  and  $\Delta n = 2$  it holds for  $n' \geq 1$ , and now is  $\alpha < 0$ .

In the sequence  $\Delta n = -1$  it holds probably for  $n' \geq 2$  and we have  $\alpha > 0$ <sup>1)</sup>.

For the bands in a  $n''$  progression the intensity ratio is also the ratio

<sup>1)</sup> Dr. W. R. VAN WIJK pointed out to us that this exponential relation between vibrational transition probability and vibrational energy, just as the fact that in the sequences  $\Delta n = -1$ , 1 and 2 the first transition probability has a lower value than the following one, can be understood from CONDON's theory.



TABLE III.

Vibrational transition probabilities in the Cyanogen  $2\Sigma - 2\Sigma$  band system.

$n' \backslash n''$	0	1	2	3	4	5	6	7	8	Sum
0	1.0	0.055	0.003							1.06
1	0.16	0.87	0.095	0.007						1.13
2		0.29	0.77	0.12	0.009					1.19
3			0.24	0.67	0.15	0.012				1.07
4				0.20	0.59	0.19	0.016			1.0
5					0.15	0.51	0.23	0.02		0.91
6						0.13	0.46	0.29	0.027	0.91
Sum	1.16	1.22	1.11	1.0	0.90	0.84	—	—	—	

of the transition probabilities. Assuming the observed BOLTZMANN distribution temperature ( $T=5870^\circ$  abs.) for the vibrational levels, we obtain table III for the relative transition probabilities (using the by means of the straight lines in figs. 1 and 2 corrected band intensities).

The sum of each horizontal set of  $p$ -values and the sum of each vertical column represents respectively the statistical weights at infinite temperature of the initial and final levels.

From table III we see that  $\sum_{n''} p_{n'n''}$  only approximately is the same for all  $n'$  states. Using the data of table III we find the BOLTZMANN factor for each  $n'$  state in dividing the observed  $\sum_{n''} I_{n'n''}$ -values by the corresponding sum of transition probabilities. Plotting them in fig. 3 (instead of  $\sum_{n''} \frac{I}{\nu^4}$ ) against the vibrational energy, the points show no systematical deviation of the straight line corresponding to  $T=5870^\circ$  abs., even not for  $n'=5$  and  $n'=6$ .

It is of importance to extend the intensity measurements in the cyanogen band spectrum to the higher vibrational transitions; also the intensity distribution in the band systems of other molecules (under different conditions) may be investigated. Further work in this direction will be done.

## SUMMARY.

In the cyanogen  $^2\Sigma - ^2\Sigma$  band system the intensity distribution has been determined from measurements of the maximum intensities of the band heads, which seem to give the real ratio of the band intensities, as has been checked in sequence  $\Delta n = 0$ . It appeared that a distribution temperature for the vibrational levels exist, which is the same as for the rotational levels. The vibrational transition probabilities are determined, and it has been found that in each sequence (after certain value of  $n'$ ) an exponential relation exists between transition probability and vibrational energy.

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**Physics.** — *On the possibility of separating neon into its isotopic components by rectification.* By W. H. KEESOM and H. VAN DIJK.  
(Communication N<sup>o</sup>. 213a from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 31, 1931).

§ 1. *Introduction.* This investigation was begun in connection with a conversation followed by some correspondence with Professor Dr. O. STERN at the end of 1925 and the beginning of 1926.

According to an estimate made by Professor STERN the difference in vapour pressure of the two isotopes  $Ne_{20}$  and  $Ne_{22}$  (as solids) at the temperature of the triple point ( $24.57^\circ K.$ ) <sup>1)</sup> would amount to about 3 or 4 %. Further the lighter isotope would possess the higher vapour pressure. This is valid for the case when one calculates *with* zero-point energy. *Without* zero-point energy the heavier isotope would have the higher vapour pressure, and the difference would be larger, viz. about 8 or 9 % at the triple point. Professor STERN, however, considered it very probable that one must calculate with zero-point energy.

The calculations had already been made by Professor STERN before 1914, but had not been published. This was done for the first time by F. A. LINDEMANN <sup>2)</sup>. The formulae are as follows :

*with* zero-point energy :

$$\ln \frac{p_1}{p_2} = \frac{3}{40} \left( \frac{h\nu_m}{kT} \right)^2 \left( 1 - \frac{m_1}{m_2} \right) \dots$$

*without* zero-point energy :

$$\ln \frac{p_1}{p_2} = -\frac{9}{8} \frac{h\nu_m}{kT} \left( 1 - \sqrt{\frac{m_1}{m_2}} \right) + \frac{3}{40} \left( \frac{h\nu_m}{kT} \right)^2 \left( 1 - \frac{m_1}{m_2} \right) \dots$$

Here  $p$  = vapour pressure,  $\nu_m$  = limiting frequency according to DEBIJE,  $m$  = atomic weight ; the index 1 relates to  $Ne_{20}$ , the index 2 to  $Ne_{22}$  ; for  $\nu_m$  an average value can be taken. The limiting frequency  $\nu_m$  could be estimated with the aid of LINDEMANN's melting point formula <sup>3)</sup>. This gave  $h\nu_m/k = \Theta = 52$  <sup>4)</sup>.

<sup>1)</sup> C. A. CROMMELIN and R. O. GIBSON. These Proceedings **30**, 362, 1927, Comm. Leiden No. 185b.

<sup>2)</sup> F. A. LINDEMANN, Phil. Mag. **38**, 173, 1919. Cf. also K. F. HERZFELD, Müller-Pouillet's Lehrbuch der Physik, 11e Aufl., III 2, 389, 1925.

<sup>3)</sup> F. A. LINDEMANN, Physik. Zs. **11**, 609, 1910, Cf. Leiden Suppl. No. 23, p. 272 (equation (121) and footnote 845).

<sup>4)</sup> K. CLUSIUS, Zs. physik. Chem. B. **4**, 1, 1929 found  $\Theta = 63$  from direct measurements concerning the specific heats.

It would be very important if it could be stated merely whether the lighter or the heavier isotope has the higher vapour pressure, as from that distinction one can draw a conclusion about the existence or non-existence of the zero-point energy.

Professor STERN had also calculated the vapour pressure curve for mixtures of the isotopes as a function of the composition (not published). This curve appeared to be very nearly straight. This enables one to make an estimate about the difference in composition between coexisting phases: solid-vapour. According to such an estimate (calculated with zero-point energy) those two phases at the triple point would show, the solid being evaporated, a difference in density of 0.03 %. By 30 or 40 fractionations this difference might be raised to 1 %.

The formulae mentioned above have been derived for the solid state. One can expect, however, that they are valid with close approximation for the liquid state too (not too far from the triple point)<sup>1)</sup>.

§ 2. Attempts to realize a separation of neon with regard to its isotopic components have been made by ASTON<sup>2)</sup> and by G. HERTZ<sup>3)</sup>. ASTON applied diffusion through pipeclay, and obtained by an extremely laborious and prolonged series of diffusions a difference in density of 0.7 %. The results of HERTZ's experiments have not come to our notice.

Experiments made by ASTON<sup>2)</sup> to realize a partial separation by fractional distillation over charcoal at the temperature of liquid air were not successful.

We decided on the basis of the estimates mentioned in § 1 to try to obtain a partial separation by means of rectification in a rectifying column at a temperature just above the triple point. It appeared to be possible to construct a rectifying apparatus built in a Dewar glass possessing a column with 19 pans. By this means one might obtain theoretically<sup>4)</sup> in one rectification a difference in density of about 0.5 % between the lowest and uppermost portions in the rectifying column<sup>5)</sup>. In reality one will have to reckon with an efficiency factor of say 50 %, so that one could expect only a difference of about 0.25 %<sup>6)</sup>.

As yet we have made three rectifications with such an apparatus (§ 3). The first two did not give absolutely certain results. The last one fully fulfilled the expectations. We obtained a difference in density of 0.4 %.

1) Cf p. 49 note 1.

2) F. W. ASTON, *Isotopes*, London 1924, p. 43.

3) G. HERTZ, *Physik. Zs.* 23, 433, 1922. *These Proceedings* 25, 434, 1922. *Zs. f. Physik* 19, 35, 1923.

4) Calculating now with  $\theta = 63$  (cf. note 4 p. 42) and assuming that the rectifying process has lasted indefinitely long (cf. § 7).

5) In this communication we neglect the small quantity of  $Ne_{21}$  that is contained in normal neon.

6) By slowly drawing off vapour the difference between a quantity collected at the beginning and another one collected at the end of the process might still become larger.



The experiments will be continued on a proper scale with an apparatus which will be somewhat modified on account of the experience obtained. We so hope to obtain mixtures with sufficient difference in the ratio of the components so that it will be possible to experiment with them and obtain a knowledge based on experimental data concerning the difference in behaviour of the isotopes.

Meanwhile it seemed to us to be of some interest to publish the results obtained, as it has already become certain that of the two isotopes the lighter one has the higher vapour pressure. According to the considerations mentioned in § 1 this means that we have to reckon with zero-point energy. We shall come back to this in § 7.

§ 3. *The rectifying apparatus* (Figs. 1 and 2 on the following page) consists of the copper condenser  $R_H$ , the rectifying column  $C$  (German silver, with copper pans), and the still  $B$  (copper).

The rectifying column contains 19 pans which hold 5 cc of liquid each. The still has a volume of about 600 cc.

The neon enters from gasholders through  $I_{Ne}$  and reaches after a preliminary cooling between the windings of the spiral  $S_p$  the condensation space  $R_c$ . Here it is condensed against the wall of the space  $R_H$ , in which hydrogen is evaporated. The hydrogen vapour flows through the spiral  $S_p$  and leaves the apparatus through  $U_H$ .

A small helium thermometer is fastened against the wall of  $R_H$  at the beginning of the spiral  $S_p$  in order to control the temperature, especially to take care that the temperature will not get too low there, as then the neon would solidify against the wall.

The condensed neon drops down and fills successively the pans and the still  $B$ . This contains also a helium thermometer  $T_2$ , which i.a. indicates when the neon begins to condense, or when the still begins to get empty.

To control the temperatures of the rectifying column two thermoelements (copper-constantan),  $T_3$  and  $T_4$ , have been soldered to it. The temperature of the condensing neon is controlled by means of a mercury manometer, which is in connection with  $R_C$  (through  $I_{Ne}$ ). The temperature or pressure difference between the still and  $R_C$  can be controlled continuously with a differential manometer.

The tubes  $A_b$  and  $A_o$  enable to take off neon. Further the apparatus still contains two heating coils: one,  $S_1$ , round the rectifying column, another,  $S_2$ , against the bottom of the still. They have each 30 Ohm resistance. The first heating coil serves eventually to evaporate the liquid of the column into a separate container, the other to maintain the rectification.

The whole apparatus is built within a Dewar glass  $D$ . The space between the apparatus and the glass can be filled with neon.

§ 4. *Purity of the gas.* The neon was kindly put at our disposal by the PHILIPS' Lampworks. We also here tender our best thanks to that firm

and to chem. docts. H. FILIPPO, chief Engineer of that firm, for their kind assistance.

The gas originally contained 60 to 30 % admixture, principally nitrogen

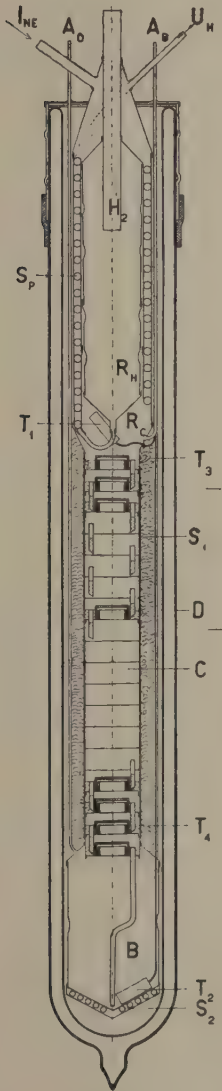


Fig. 1.

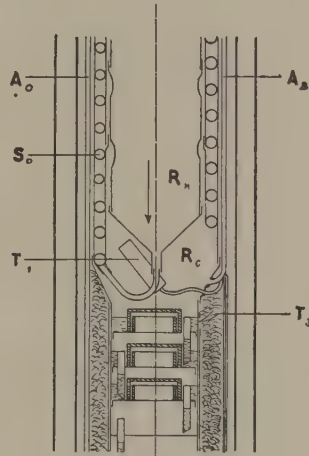


Fig. 2.

and helium. We purified it by freezing out with liquid hydrogen and by fractional evaporation. So we obtained 1000 l. neon that contained less than 1 % nitrogen and only very little helium or hydrogen. It was stored in three gasholders.

We had to make extraordinary demands of purity on those fractions taken from the rectification products, which were destined for the gas density determinations.

If the rectified neon is already nearly free from nitrogen at the outset then the danger will be small that the fractions taken off at  $-248^{\circ}$  C. will contain any nitrogen at all. Also the heavier fraction will not easily contain the more volatile impurities, as by the rectification process these will be eliminated from them. In the light fraction one can, however, rather expect impurities in weighable amount, especially hydrogen.

To eliminate the last quantities of impurity from the fractions destined for the gas density determination we applied two methods:

a. repeated condensation by means of liquid hydrogen and fractional evaporation;

b. absorption of the impurities by chabasite at the temperature of liquid air.

The purity of these neon fractions was controlled by spectrum analysis (large Steinheil spectrograph). Direct application of this method does not give a sensitive test concerning the presence of nitrogen<sup>1)</sup>. By examining the deposit which remains after evaporation at liquid hydrogen temperature the purity of the sample can be tested many times more accurately. On the other hand, an extremely small quantity of admixed hydrogen gives rise to the hydrogen lines; so the judgment whether hydrogen is present in a weighable quantity is difficult<sup>2)</sup>.

By application of LILIENFELD's<sup>3)</sup> method we could still detect an admixture of 0.3 % helium. If, however, the neon is once spectrum-analytically free from helium, as was the case already before the first rectification, one can be rather sure that after some rectifying and removal of the more volatile products the remaining neon will no longer contain any helium.

§ 5. *Gas density determinations.* These were made by weighing the gas in bulbs. We used 3 bulbs, one of 283 cc, the other two of 760 cc each. We used two counterpoise bulbs with very nearly the same volumes.

For determining the constants of a density bulb we measured the difference in weight between the counterpoise bulb and the density bulb when the latter was filled with oxygen, and then when it was filled with hydrogen. The pressure was in each case nearly atmospheric. So we avoided a correction in consequence of the contraction of the bulb with change of inner pressure. Pressure and temperature were measured very exactly before closing the bulb.

For the normal densities of oxygen and hydrogen we took:

oxygen: 0.0014290,    hydrogen: 0.0000899.

1) The nitrogen bands are barely visible in mixtures of neon with 2 % air.

2) According to H. KAYSER, *Handb. d. Spectroscopie* I, 246, Leipzig 1900, 0.001 % hydrogen is still clearly visible in helium.

3) J. E. LILIENFELD, *Ann. d. Phys.* (4) 16, 931, 1905.

The weighings were accurate to  $\frac{1}{50}$  mg. We used a BUNGE physical-analytical balance. The weights were tested on a balance especially built for us by that firm.

§ 6. *The rectifications.* Up to the present we have made 3 rectifications. They principally served to study the process and to gain data concerning a further separation of neon by means of fractional rectification.

As the results of the two first rectifications for various reasons were not in all respects satisfactory, we shall communicate only the details and the results of the last one.

This took place on Oct. 22 and 28, 1930. It was performed with 700 l. neon, which before this experiment was again purified very carefully. The density at standard conditions of this initial neon we estimate to have been 0.0009000, if we put the standard density of normal neon at 0.0008999<sup>1)</sup>.

In the first rectification we had drawn off from the original quantity of 1000 l. normal neon a fraction of 130 l. that had a density of 0.00089939. This gives for the remaining neon, of which the 700 l. now used formed part, the density mentioned above.

The aim of this rectification was to obtain a distillate which was lighter, as well as one which was heavier than normal neon.

We met with rather great difficulties in keeping the difference in temperature (pressure) between the condensation space and the still constant during the long interval of time required. This requires an uninterrupted uniform supply of liquid hydrogen. Also the escape of the hydrogen vapour had to go on regularly. These difficulties were largely overcome by supplying the liquid hydrogen from a bulb, which itself was kept filled from a steadily renewed hydrogen bulb, and by regulating the escape of the hydrogen vapour by means of a flowmeter and a regulating valve. In this third rectification we used as far as possible containers of 15 l. for the supply of liquid hydrogen at those times when a lengthy constant condition was required. So we could keep the condition constant for a period of 3 hours.

To diminish the chance of an obstruction towards the end of the rectification we divided it in two periods. These two periods lasted 14 hours each.

In the first period we first rectified 6 hours without taking off anything. We then took a sample (4 l.) from the condensation space: fraction  $D_6$ . Thereafter we drew off 250 l. from the condensation space during 8 hours. We evaporated the remaining 450 l. into one container.

We rectified the last mentioned quantity anew in the second period. We now reduced the preliminary period (rectifying without taking off) to  $3\frac{1}{2}$  hours. During the following 5 hours we took off 180 l. During the

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<sup>1)</sup> G. P. BAXTER and H. W. STARKWEATHER. Proc. Nat. Acad. Washington, 14: 50, 57, 1928.



last 5 hours we again did not draw off anything. At the end of this period we took a sample from the still: fraction  $D_7$ .

The whole process with the preliminary cooling of the apparatus included had required 200 l. liquid hydrogen.

$D_6$  as well as  $D_7$  were condensed 3 times by means of liquid hydrogen, and each time divided into 3 fractions in evaporating, taking always the middle fraction. Moreover  $D_6$  was purified by absorption in chabasite to eliminate hydrogen that eventually might be present still <sup>1</sup>). The two large density bulbs were filled with  $D_6$  and  $D_7$  respectively, the small one with  $D_7$ .

Results of the gas density determinations:

$$D_6: S_{06} = 0.000\ 898\ 30,$$

$$D_7: S_{07} = 0.000\ 902\ 11 \text{ (large bulb),}$$

$$S'_{07} = 0.000\ 902\ 18 \text{ (small bulb).}$$

$S_0$  means density at standard conditions. Spectrum analysis showed, that the intensity of the hydrogen spectrum in  $D_6$  was only weak. After a short time it totally disappeared (by absorption in the discharge tube).

Hence we obtained with this rectification a plain partial separation. Although the results obtained with the first two rectifications were less certain, they all lie in the same direction.

§ 7. *Efficiency of the rectifying column.* If we suppose that the rectifying column were 100 % efficient, viz. that the vapour rising from a pan is in thermodynamic equilibrium with the liquid, we should obtain, according to STERN's formulae (§ 1) with  $\Theta = h\nu_m/k = 63$ , at the triple point,  $x'_{19} = 0.044$  and  $x''_0 = 0.094$ , if at the outset  $x = 0.090$ ,  $x''_0$  being the composition (in terms of  $Ne_{22}$ ) of the liquid in the still,  $x'_{19}$  being the composition of the vapour above the 19<sup>th</sup> pan (i.e. in the condensation space) <sup>2</sup>).

We have to consider, however, that in the time the experiment lasted the stationary condition cannot have been reached. The period of adjustment of the rectifying column is governed by the following relation <sup>3</sup>):

$$t_m = \frac{4}{\pi^2} \frac{(n+1)^2 l}{r} \ln \frac{8}{\pi^2} m.$$

<sup>1</sup>) Cf. G. GLAUDE, C.R. 158, 861, 1914. S. VALENTINER and R. SCHMIDT, Ann. d. Phys. (4) 18, 187, 1905.

<sup>2</sup>) We took into account that the quantity of liquid in the still =  $6 \times$  the total quantity on the pans.

<sup>3</sup>) In deriving this formula we supposed that the column efficiency is 100 %, that for the different pans  $x' - x''$  may be put the same ( $x'$  = composition of the vapour,  $x''$  = composition of the liquid), that  $r$  remains constant over the whole column, and that the quantity of liquid in the still is so large that the composition does not change there.

Here  $n$  = the number of pans,  $l$  = the quantity of liquid on one pan,  $r$  = the quantity of vapour circulating per unit of time,  $t_m$  = the time elapsing from the outset, at which the composition was everywhere the same, to the moment at which the stationary condition has been reached except for  $1/m^{\text{th}}$  part.

For the rectification described in § 6 :  $l = 5$  cc,  $r = 3$  cc/min,  $n = 19$ . For  $t_m = 360$  min we find  $m = 4.65$ . This gives  $x'_{19} = 0.054$  and  $x'_0 = 0.093$ . Hence follows a difference in density of 0.36 % with the initial neon.

We found a difference in density between  $D_6$  and the initial neon of 0.19 %. Hence follows for the efficiency of the column at the velocity of circulation used the value 53 %.

As in industry one reckons also with an efficiency of that order of magnitude we may conclude that the result of this rectification wholly meets the expectation.

If we accept this value of the efficiency for the continuation of the process till the drawing off of  $D_7$ , we calculate for the difference in density between this fraction and the outset neon a value of 0.3 %. In reality it was 0.23 %. The difference is to be ascribed to different small deviations from the theoretically normal course of the process, so that this result too may be considered to have met the expectation.

§ 8. *Zero-point energy in the solid state.* The results of the rectification described in § 6 show that the vapour phase has a larger content of the lighter isotope of neon than the liquid phase. From this follows that  $Ne_{20}$  has a higher vapour pressure than  $Ne_{22}$  (at 24.7° K.).

We may accept as very probable, that also for the solid condition  $p_{20} > p_{22}$ <sup>1)</sup>. Further that  $p_{20}/p_{22}$  should approximate to 1 if the temperature could be raised high enough. We conclude that very probably  $d/dT \cdot \ln p_{20}/p_{22} < 0$ . Hence follows :

$$\lambda_{20} < \lambda_{22},$$

and from this

$$U_{20} < U_{22},$$

if  $\lambda$  = heat of vaporisation,  $U$  = internal energy, both per gramme atom. DEBIJE's theory for the solid state tells that this is so only if one accepts zero-point energy.

§ 9. *Summary.* Neon was rectified at a temperature of  $-248.4^\circ$  C. We found that the lighter isotope is more volatile than the heavier one.

From this it follows to a large degree of probability that the solid state possesses zero-point energy.

<sup>1)</sup> One derives from the value of the melting heat that this should not be valid if the triple point of  $Ne_{22}$  should lie 0.5 degree or more below that of  $Ne_{20}$ . Presumably it lies, however, above.

We measured the following gas densities :

$D_6$  (light fraction):  $S_{06} = 0.000\ 898\ 30$ ,  $A = 20.14$ ,

$D_7$  (heavy „ ):  $S_{07} = 0.000\ 902\ 11$ ,  $A = 20.23$ ,

the same:  $S'_{07} = 0.000\ 902\ 18$ .

In calculating the atomic weight we accepted 20.18 for that of normal neon.

Finally we are pleased to record our thanks to Mr. N. BRUNT, chem. cand., and Mr. J. HAANTJES, phil. nat. cand., for their help at the rectifications and the purification of the samples for weighing, to Mr. G. J. FLIM, chief of the technical staff of the Cryogenic Laboratory, for his help at the construction of the rectifying apparatus, and to Mr. A. OUWERKERK, technician 1<sup>st</sup> class of this laboratory, for his help in the treatment of the neon.

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**Physics.** — *Measurements of the electrical resistance of pure indium, thallium and gallium at low temperatures and of the magnetic disturbance of the supraconductivity of thallium.* By W. J. DE HAAS and J. VOOGD. (Comm. N<sup>o</sup>. 212d from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 31, 1931).

§ 1. *Introduction.* The change of the electric resistance of indium and thallium at very low temperatures has been investigated by W. TUYN and H. KAMERLINGH ONNES<sup>1)</sup>.

For our investigations on the magnetic disturbance of the supraconductivity we had at our disposal resistances of very pure indium and thallium and the spectroscopically pure gallium. Our measurements gave the definite result that this last metal too belongs to the superconductors<sup>2)</sup>.

We investigated the resistance of these pure metals and of thallium the longitudinal magnetic disturbance of the supraconductivity at different temperatures.

§ 2. *Indium.* We used the resistance *In-1-1928*, made of very pure indium from Ad. Hilger Ltd., London. For the measurements short indium wires were soldered to its extremities. We measured the resistance at the boiling point of helium and at some temperatures in the neighbourhood of the transition point of indium. In table 1 we give the values of the resistances divided by the resistance at 0° C. ( $R/R_0$ ) for these temperatures.

The temperatures were derived from the vapour pressures of the helium bath with the aid of the vapour pressure curve<sup>3)</sup>.

TABLE 1. *In-1-1928.*

$T^{\circ}\text{K.}$	$p_{\text{helium}}$ in mm Hg.	$R/R_0$
4.24	774	0.00904
3.38	311.5	0.00894
3.37	310.2	0.00204
3.37	309.4	0

1) Comm. Leiden N<sup>o</sup>. 167a.

Comm. Leiden N<sup>o</sup>. 160a.

2) Comm. Leiden N<sup>o</sup>. 199d.

3) W. H. KEESOM, SOPHUS WEBER and G. SCHMIDT, Comm. Leiden N<sup>o</sup>. 202c.



In order to make comparisons with earlier measurements easy we give the vapour pressures separately. The value  $R/R_0$  at the boiling point of helium is 0.00904 and the resistance vanishes between 311 and 309 mm. pressure of the helium vapour.

For the purest indium, investigated by TUIJN and KAMERLINGH ONNES the value of  $R/R_0$  was 0.03390 at the boiling point of helium and its resistance vanished between 309 and 305 mm pressure of the helium vapour. The transition point evidently rises somewhat when the purity is increased.

For *In-1-1930* the resistance vanishes within a smaller temperature interval than for the indium samples examined previously. Probably this has to do with the monocrystalline character of *In-1-1930* which became evident by the investigation of the magnetic disturbance<sup>1)</sup>.

§ 3. *Thallium*. We made a wire by pressing the liquid thallium, obtained in a pure state from Ad. Hilger Ltd., into a glass capillary. This capillary tube was somewhat wider at the extremities into which two platinum wires were melted.

After crystallisation of the liquid thallium we called this resistance *Tl-1-1930*. The tube was hermetically closed so that the thallium could not oxidize.

We determined the change of this resistance in liquid hydrogen and in liquid helium. The results of the measurements have been given in table 2.

The value  $R/R_0$  at the boiling point of helium is somewhat lower than in the case of the purest sample examined by TUIJN and KAMERLINGH ONNES.

The transition point however is the same.

TABLE 2. *Tl-1-1930*.

$T^{\circ}\text{K.}$	$p_{\text{helium}}$ in mm Hg.	$R/R_0$
20.41		0.03051
18.06		0.02298
16.21		0.01765
14.24		0.01263
4.22	759	0.000537
2.38	60.1	0.000408
2.35	56.9	0

§ 4. *Gallium*. From the pure gallium, kindly put at our disposal by Prof. JAEGER, Groningen, we made some resistances, one of which was *Ga-5-1928*.

<sup>1)</sup> Comm. Leiden N<sup>o</sup>. 187d.

For the measurements copper wires were welded to the gallium wire.

The results of the resistance measurements between  $91^{\circ}$  K. and  $4^{\circ}$  K. have been given in table 3. In a previous paper we communicated already

TABLE 3. Ga-5-1928.

$T^{\circ}\text{K}$	$R/R_0$
90.55	0.2625
74.83	0.1925
57.07	0.1170
20.43	0.00906
18.72	0.00687
16.58	0.00462
14.04	0.00265
4.23	0.00031

the change of the resistance of this pure gallium below  $4^{\circ}$  K. and especially its vanishing between  $1^{\circ}.07$  K. and  $1^{\circ}.05$  K.<sup>1)</sup>

§ 5. *Investigation of the longitudinal magnetic disturbance of the superconductivity of pure thallium.* W. TUYN investigated already the temperature dependance of the transverse magnetic disturbance of the superconductivity of thallium<sup>2)</sup>.

We extended this research by measuring for different temperatures the longitudinal disturbance for the resistance *Tl-1-1930*. The results of the measurements are to be found in table 4.

In an increasing magnetic field the resistance is restored to its normal value within a small range of field intensity. If the field is again decreased, first a wide hysteresis shows itself and then the resistance vanishes discontinuously in a few steps.

The character of the transition figure suggests the idea that the resistance *Tl-1-1930* has a monocrystalline structure. We did not investigate this in detail.

In table 4 we also give the value of the magnetic field for which in an increasing field the resistance is restored to half of its normal value ( $HW^{1/2}$ ).

As was found in an other investigation the value of this field is very useful to indicate the way in which the magnetic disturbance depends on

<sup>1)</sup> Comm. Leiden N<sup>o</sup>. 199d.

<sup>2)</sup> Comm. Leiden N<sup>o</sup>. 191b.

TABLE 4. Tl-1-1930.

$\bar{H}$	$R$	Remarks	$T^{\circ}\text{K.}$	$P_{\text{helium}}$ in mm. Hg.	$HW^{1/2}$
31.2		resistance comes back	2.13	34.4	31.4
31.4	0.000056				
31.7	072				
32.1	108				
34.2	110				
42.8	108				
31.7	108				
30.8	110				
28.3	0	resistance vanishes suddenly			
68.5	0		1.78	12.4	70.0
70.0	0.000036				
70.6	109				
75.0	107				
85.6	109				
128.4	108				
68.5	109				
66.3	109				
64.4	0	resistance vanishes suddenly			
85.6	0		1.56	5.6	91.6
91.6	0.000061				
92.4	108				
96.3	108				
128.4	108				
87.7	108				
85.6	0	resistance vanishes suddenly			
110.0		resistance comes back	1.35	2.05	110.6
110.6	0.000053				
111.3	108				
171.2	108				
109.1	108				
104.4	0	resistance vanishes suddenly			

the temperature<sup>1)</sup>). The measured half values are plotted in fig. 1 against the temperature. For comparison we calculated the same values for mercury

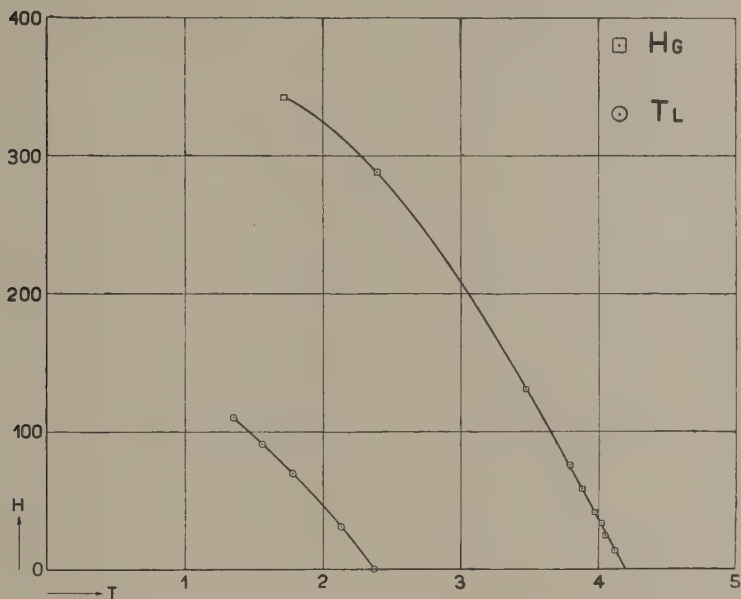


Fig. 1.

from measurements of W. J. DE HAAS, G. J. SIZOO and H. KAMERLINGH ONNES, the temperatures of which we corrected with the aid of the new vapour pressure curve for liquid helium<sup>2)</sup>).

For mercury the curve magnetic half value — temperature begins at the transition point as a straight line, but below 3° it is curved more and more towards the temperature axis.

For thallium this curvature sets in directly below the transition point already.

Therefore the cause of the curvature is present in mercury below 3° K. only and in thallium is already present at the transition point.

We gladly express our thanks to Mr. J. M. BLOM for his help during the measurements.

<sup>1)</sup> Comm. Leiden N°. 212c.

<sup>2)</sup> Comm. Leiden N°. 180d.



**Physics.** — *Further investigations on the magnetic disturbance of the supraconducting state of alloys.* By W. J. DE HAAS and J. VOOGD.  
(Communication N<sup>o</sup>. 214b of the Physical Laboratory Leiden.)

(Communicated at the meeting of January 31, 1931).

§ 1. *Introduction.* In previous papers we have already discussed several measurements of the magnetic disturbance of the supraconducting state of alloys <sup>1)</sup>. We found as a general rule that per degree decrease of temperature the magnetic transition curve is shifted more towards the higher field intensities for the alloys than for the pure metals.

The most striking example of this is the eutectic of the system lead-bismuth. At 4°2 K this alloy is still supraconductive in a magnetic field of 14000 Gauss and at 1°9 K still in a field of 20.000 Gauss.

We continued these investigations with some other lead alloys and with the eutectic of the system gold-bismuth. These lead alloys were solid solutions of 15 % mercury in lead, of 40 % thallium in lead and of 35 % bismuth in lead.

§ 2. During the making of homogeneous solid solutions, the complication arises that the liquid mixture crystallizes inhomogeneously. This is because of the fact that at different stages of the crystallization the liquid mixture is in equilibrium with solid solutions of different constitutions. In the condensation nuclei therefore a solution of definite composition crystallizes and round them layers of solid solutions of different concentration are formed as the temperature is lowered. Generally these solid solutions are made homogeneous by slow congelation. Afterwards the mass is cleared from the still subsisting inhomogeneities in the following way. It is rolled and welded repeatedly so that it becomes very finely divided. Then it is heated during a long time just below the temperature of first formation of liquid. Then the last inhomogeneities must disappear by diffusion.

For our investigations this procedure has the great disadvantage, that the required mechanical processes are too dangerous for the purity of the metal.

That is why we worked out another method. We dripped namely very small drops of liquid of the right composition on a cooled metal block, where they are directly congealed. In this way a rod of the alloy is formed by the accumulated drops. Each of these congealed drops was inhomogeneous to the same degree and because of the small dimensions

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<sup>1)</sup> Comm. Leiden N<sup>o</sup>. 199c, Comm. Leiden N<sup>o</sup>. 208b.

of the drops only a short time was required to make the rod homogeneous by diffusion.

The dripping of the liquid was effectuated in the following way. The metal of the required composition was contained in a thickwalled vertical glass tube *A* (fig. 1), which ended in a narrow opening of about 0.05 mm diameter. Round this tube *A* a second tube *B* was placed, which could be evacuated. At the height of the metal mixture and of the small orifice an electric resistance furnace (*C*) was placed round the surrounding tube and in the closed lower end of the latter a copper block *D* was placed, which was cooled by liquid air.

The metal mixture was melted and then the surrounding tube was evacuated. Now the liquid was pressed through the narrow orifice by means of carbonic dioxide of about 40 atm. Drops were formed of a few hundredths of a millimeter diameter, which were not solidified before they fell on the cold copper block or on the rod in formation.

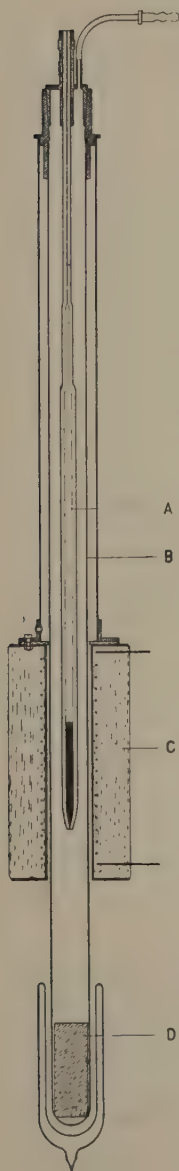
We found an opening of about 0.05 mm to be very suitable for a pressure of 40 atm. A larger opening gives larger drops and so great a flux of metal, that the drops are not directly solidified on the block. With the same pressure a smaller opening makes the flux of the metal so weak, that at the opening the small drops are clustering together to large ones, which fall down as a whole.

For preliminary investigations with solid solutions we did use this wearisome procedure. The solid solution of 15 % mercury in lead and of 40 % thallium in mercury are made by cooling down very slow the liquid mixture.

The more extensive procedure has been used however for the preparation of solid solutions of bismuth in lead, both for those of 7 %, of 10 % and of 20 % bismuth in lead described in the preceding communication and for those of 35 % bismuth in lead the measurements with which will be discussed in this paper.

In the case of the latter alloy the rod was first made homogeneous by diffusion, then a wire was made by pressing it while cold; finally it was heated again during some time.

In order to control the method we made two resistances from different pieces of such a wire and determined for both the ratio of the



resistances at the boiling point of oxygen and at 20°. These ratio's (about 0.7) were the same within 1 %.

### § 3. *Investigation of a solid solution of 35 % bismuth in lead.*

Of the system lead-bismuth we had investigated already the eutectic, in which the solid solution of bismuth in lead represented the only supraconductive phase.

For the percentage of bismuth in this solid solution, however, different values are given.

For our measurements it was necessary to know this percentage as accurately as possible. From the above mentioned investigations on solid solutions of 7 %, 10 % and 20 % bismuth in lead we knew that for a definite temperature the magnetic half value increases with the percentage of bismuth. For the solid solution with 20% bismuth the half value of the eutectic is not yet reached. Therefore the solid solution in the eutectic must have a higher percentage of bismuth than 20%. This is in agreement with some determinations of the melting point diagram of the system lead-bismuth which give for the percentage of the eutectic 35%.

That is why we made a homogeneous rod of the solid solution of 35% bismuth in lead with the procedure described above. For this rod we determined for different temperatures the transverse magnetic disturbance. The results are given in table 1.

Small deviations from the results of the measurements with the eutectic are found. These may be caused however by the complicated nature of the magnetic disturbance in the eutectic in which the current has to find its way through the layers of the supraconductive solid solution in the rod. This is namely the reason why the transverse disturbance cannot be measured purely for the eutectic, while for the homogeneous solid solution this is very well possible.

Still the quantitative agreement of the results is sufficient to allow the conclusion that the supraconductive solid solution in the eutectic contains about 35% bismuth.

### § 4. *Investigation of a solid solution of 40 % thallium in lead.*

Of the system thallium-lead we had already investigated the solid phase, the composition of which is represented by the formula  $PbTl_2$  and which becomes supraconducting at 4°09 K. Of a solution of 40% thallium in lead we expected the transition point to lie higher, so that in the helium region a considerable magnetic field would be required for the magnetic disturbance.

The rod was prepared by slow cooling and probably was still inhomogeneous. The results of the measurements are given in table 2.

The magnetical half value increases with about 1500 Gauss per degree decrease of temperature.

TABLE 1. *Pb-Bi* (35 % *Bi*).

<i>H</i>	<i>R</i>	<i>T</i> ° K	<i>P</i> <sub>helium</sub> in mm Hg	<i>HW</i> <sup>1/2</sup>
14550	0	4.22	763	18450
15450	0.000081 $\Omega$			
16750	136			
17800	516			
19200	1389			
20150	1675			
21150	1765			
22750	1809			
24200	1820			
26000	1822			
20150	1700			
17800	689			
17800	0	3.36	306	22050
19900	0.000075			
21150	421			
22100	963			
23300	1498			
25000	1748			
26000	1799			
27300	1817			
21150	472			
20450	0.000008	2.94	170	23450
22100	254			
24200	1311			
26000	1687			
27300	1783			
17800	0	2.43	68.3	24300
21150	0.000004			
22100	28			
24200	554			
26000	1388			
27300	1648			
22100	0.000002	1.97	22.9	25700
24200	234			
26000	1068			
27300	1459			
21150	0	1.88	16.9	26250
22100	0.000006			
23300	26			
25000	305			
26000	1325			



TABLE 2. *Pb-Tl* (40% *Tl*).

<i>H</i>	<i>R</i>	<i>T</i> ° K	<i>P</i> <sub>helium</sub> in mm Hg	<i>H W</i> <sup>1/2</sup>
2300	0	4.23	765	3050
3050	0.000255 $\Omega$			
3800	447			
5300	500			
7500	524			
4500	0	2.93	168	5000
5300	0.000368			
6050	454			
7500	498			
11150	533			

## § 5. Investigation' of a solid solution of 15% mercury in lead.

This solid solution was also prepared by slowly cooling down the liquid mixture. The results of the measurements are to be found in table 3. The

TABLE 3. *Pb-Hg* (15% *Hg*)

<i>H</i>	<i>R</i>	<i>T</i> ° K	<i>P</i> <sub>helium</sub> in mm Hg	<i>H W</i> <sup>1/2</sup>
6500	0	4.23	765	6800
7500	0.000321 $\Omega$			
8250	548			
9000	579			
11150	612			
8950	0	2.93	168	10300
10450	0.000123			
11850	539			
13300	586			
14550	605			

magnetical half value increases with about 2700 Gauss per degree decrease of temperature.

§ 6. *Investigation of the eutectic of the system gold-bismuth.*

Finally we investigated the eutectic of the system gold-bismuth. For this purpose we used the resistance *Au-Bi* II the supraconducting state of which had been examined already in collaboration with EDM. VAN AUBEL <sup>1)</sup>.

The magnetic fields were parallel with the axis of the rod. They were generated by a solenoid placed round the helium cryostat. The results of the measurements are given in table 4. In the preceding cases we com-

TABLE 4. *Au-Bi* II.

$H$	$R$	$T^{\circ} K$	$P_{helium}$ in mm Hg	$HW^{1/2}$
42.6	0.000050 $\Omega$	1.54	5.0	95
63.8	481			
77.8	1020			
100.2	1963			
149.8	3134			
199.6	3612			
100.3	2021			
72.0	0	1.25	1.1	147
96.2	0.000273			
146.6	1786			
170.4	2454			
199.2	3041			
96.8	309			

pared the decrease of the magnetical half value with the temperature with that found for the pure supraconductive component of the alloy.

In the case of the eutectic however this is not possible, as it contains no supraconductive component.

The only thing we can do is to compare the decrease of the magnetic half value with that found for other pure supraconductors in the same temperature region e. g. for thallium.

We then find, that also an alloy of two non supraconductors shows a greater shift of the transition figure towards the high fields than a pure supraconducting metal.

<sup>1)</sup> Leiden Comm. 197a.

### § 7. Summary.

As result of our investigations we may give the rule: At a decrease of temperature the magnetic transition figure is more shifted towards the high fields for combinations than for pure metals. The validity of this rule has been proved for the:

- 1<sup>st</sup> solid solution of bismuth in tin,
- 2<sup>nd</sup> " " " cadmium " "
- 3<sup>rd</sup> " " " 7 % bismuth in lead,
- 4<sup>th</sup> " " " 10 % " " " "
- 5<sup>th</sup> " " " 20 " " " "
- 6<sup>th</sup> " " " 35 " " " "
- 7<sup>th</sup> " " " 40 " thallium " "
- 8<sup>th</sup> " " " 15 " mercury " "
- 9<sup>th</sup> " " " 4 " bismuth " gold,
- 10<sup>th</sup> compound  $Bi_5Tl_3$ ,
- 11<sup>th</sup> "  $Sb_2Tl_7$ ,
- 12<sup>th</sup> "  $Sb_2Sn_3$ ,
- 13<sup>th</sup> "  $PbTl_2$ ,
- 14<sup>th</sup> eutectic bismuth-lead-tin,
- 15<sup>th</sup> " " " " " -cadmium.

The highest field not disturbing the supraconductivity was observed for the solid solution of 35 % bismuth in lead at 1°88 K and amounted to 21150 Gauss.

Finally we wish to express our thanks to Mr. H. BRUINING for his help during the measurements.

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**Physics.** — *The magnetic disturbance of the supraconductivity of single-crystal wires of tin.* By W. J. DE HAAS and J. VOOGD. (Communication N<sup>o</sup>. 212d from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 31, 1931).

§ 1. *Introduction.* The investigation of the magnetic disturbance of the supraconductivity revealed two peculiarities which have been examined already in detail for mercury<sup>1)</sup>.

1<sup>st</sup>. Hysteresis.

The resistance comes back in a field higher than that in which it vanishes.

2<sup>nd</sup>. Discontinuities.

For mercury resistances in a field parallel with the axis of the wire it was found that in a decreasing field the resistance vanished with a few discontinuous steps which were lying at little differing fields. Between two steps the resistance remains constant. In an increasing field the resistance is restored in a continuous way. These discontinuities were ascribed to the sudden vanishing of the resistance of the few crystallites which constituted the wire.

A general remark was also made already on the intimate connection between the state of crystallization of the material and the magnetic transition figure. We pointed especially to the desirability of the investigation of the magnetic disturbance with single-crystalline wires.

Some preliminary experiments with single-crystalline wires have been made already<sup>2)</sup>.

The results did not agree however which probably is due to disturbances of the single-crystalline state of the wires.

We continued these researches with single-crystalline wires of white tin, the single-crystalline character of which had been controlled carefully. Namely we used wires, for which we had investigated the supraconductivity<sup>3)</sup>. The dimensions of the wires had been chosen for this research especially.

The length should not be too great, as otherwise the magnetic field generated by a solenoid would not be homogeneous over the whole length. The diameter had to be small, so that accurate resistance measurements with weak currents might be possible. A strong measuring current namely

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<sup>1)</sup> G. J. SIZOO, W. J. DE HAAS and H. KAMERLINGH ONNES, Comm. Leiden N<sup>o</sup>. 180 c.  
W. J. DE HAAS, G. J. SIZOO and H. KAMERLINGH ONNES, Comm. Leiden N<sup>o</sup>. 180 d.

<sup>2)</sup> G. J. SIZOO, W. J. DE HAAS and H. KAMERLINGH ONNES, Comm. Leiden N<sup>o</sup>. 180 c.

<sup>3)</sup> Comm. Leiden No. 214 a.



would give rise to its own disturbing magnetic field, which would complicate the phenomena.

The following dimensions were found suitable, length about 15 mm, diameter from 0.15 mm to 0.25 mm.

We investigated the magnetic disturbance in magnetic fields parallel with the axis of the wires (longitudinal disturbance) and in fields perpendicular to this axis (transverse disturbance).

## § 2. *Longitudinal disturbance.*

For different wires the longitudinal magnetic transition curve was determined; it showed the same character as that in the former case. When the field is increased the resistance always comes back for a definite value of the field intensity within a small magnetic range. The rising line is therefore a steep curve, which begins straight and is somewhat curved at the upper end. When the resistance is restored to its normal value a further increase of the field does not change it anymore (but for the increase of the resistance in much higher fields).

In a decreasing field the resistance first keeps its normal value, also in fields lower than those of the rising part of the curve, until it vanishes discontinuously in one step.

Several repetitions of the cycle at the same temperature showed that the resistance always comes back in the same field. The discontinuous vanishing of the resistance however does not always take place at the same field intensity.

The latter intensities can differ considerably.

We could however not yet find the cause of this phenomenon.

The character of the transition curve is proved to be independent of the strength of the measuring current, if the latter is not too high.

In table 1 and in fig. 1 we give an example of curve of the longitudinal transition, which distinctly shows the characteristic features.

TABLE I. *Sn* — 12 — '28.  
 $T = 2.92^\circ \text{ K.}$  Longitudinal field.

<i>H</i>	<i>R</i>	Remarks	<i>H</i>	<i>R</i>	Remarks
100.4	0		100.6	0	
103.6	0.0000298 $\Omega$	jump	103.6	0.0000288 $\Omega$	jump
104.9	323		104.2	323	
107.0	323		105.7	323	
89.9	323		99.9	0	jump
89.2	0	jump			

The rising and the descending parts of the curve differ in two important points :

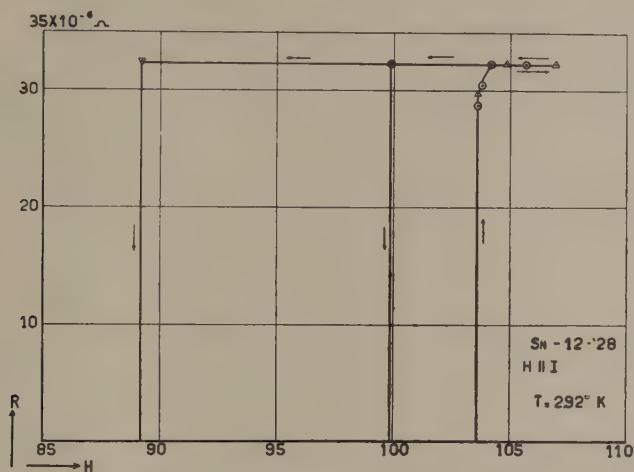


Fig. 1.

1<sup>st</sup>. On the rising part it is possible to realise transition states between normal resistivity and supraconductivity; on the descending part this is impossible.

2<sup>nd</sup>. The rising part of the line always lies at the same intensities of the field, the descending part not, though always at lower intensities than the rising curve.

### § 3. Transverse disturbance.

In this case the curve of the magnetic transition shows a character quite different from that described above.

In an increasing field the resistance comes back continuously within a magnetic range of about  $\frac{2}{3}$  of the field intensity for which the restoration of the resistance begins. The resistance has regained its normal value at about the same field intensity as has been found for the longitudinal field. In first approximation the character of the rising line is independent of the measuring current, becoming less curved only with higher measuring current.

This is not the case for the descending branch.

In a decreasing field the resistance first keeps its normal value. Then for a definite intensity of the field the resistance falls suddenly and the amount of this sudden decrease in resistance is the higher the weaker the measuring current is.

For very weak measuring currents the resistance can even vanish suddenly for a field intensity for which in an increasing field the resistance is already partially restored.

If however, after this sudden fall of the resistance there is left still part

of the resistance, this rest vanishes very slowly only in the decreasing field, so that finally the sample becomes supraconducting in a field lower than that for which in the increasing field the resistance begins to come back.

In table 2 and in fig. 2 we give an example of such a transverse transition figure.

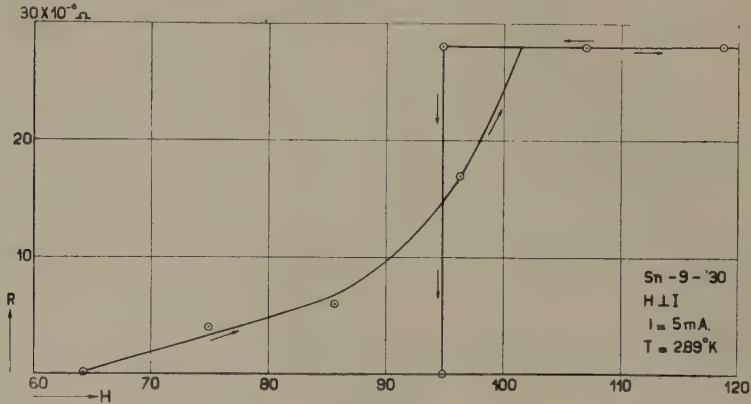


Fig. 2.

#### § 4. Discussion.

We first discussed our transition figures with a view to the question how we might still refine and complete our experiments.

a. As to the state of crystallization near the soldering places little irregularities may exist.

b. Little attention has been paid to the right orientation of the axis of the wire with respect to the magnetic field, so that deviations between this axis and the field are very well possible.

Both a. and b. may have influenced the details of our transition figure without however, in our opinion at least, doing damage to the important characteristics of the longitudinal and the transverse disturbance.

A comparison with results of earlier measurements with poly-crystalline tin wires in homogeneous fields<sup>1)</sup> supports this opinion.

Here too in the longitudinal case the resistance comes back within a much smaller magnetic range than in the transverse case. The hysteresis figure of these wires reminds one even of that found by us in our single-crystalline wires.

As to the *orientation of the crystal axis with respect to the axis of the wire*, it would be very interesting to know whether this has an influence on the magnetic disturbance.

We investigated the longitudinal disturbance for several single-crystalline wires the tetragonal axis of which was nearly exactly perpendicular to the axis of the wire. The magnetic transition figure had the same character.

<sup>1)</sup> G. J. SIZOO, W. J. DE HAAS and H. KAMERLINGH ONNES, Comm. Leiden No. 180 c.

TABLE II.  $S_n - 9 - '30$ . $T = 2.89^\circ \text{ K.}$  Transverse field.

$H$	$R$	Current	Remarks	$H$	$R$	Current	Remarks
64.2	$0.0000015 \Omega$	20 m.A.		98.4	$0.0000236 \Omega$	5 m.A.	
70.6	$4^3$			107.0	$28^1$		
77.0	$6^3$			117.7	$28^6$		
85.6	$13^2$			128.4	$28^6$		
92.0	$19^5$			149.8	$28^6$		
96.3	$23^0$			214.0	$28^6$		
102.7	$28^1$			117.7	$28^1$		
107.0	$27^8$			107.0	$28^1$		
128.4	$28^1$			96.3	$28^6$		
214.0	$28^1$			94.6	$16^6$		jump
107.0	$28^1$			92.0	$10^6$		
96.3	$28^1$			85.6	$7^5$		
94.2	$28^1$			77.0	$4^0$		
92.7	$17^7$		jump	64.2	$1^0$		
90.9	$17^0$			0	0		
89.9	$16^7$			64.2	0		
87.7	$15^2$			74.9	4		
83.5	$11^6$			85.6	6		
77.0	$8^3$			96.3	17		
70.6	$6^6$			107.0	28		
64.2	$3^3$	10 m.A.		117.7	28		
53.5	0			321.0	28		
42.8	0			117.7	28		
64.2	$1^0$			107.0	28		
70.6	$1^5$			96.3	28		
77.0	$4^0$			94.8	0		jump
85.6	$7^5$			0	0		
92.0	$15^1$			94.8	10		



Besides we investigated the transverse disturbance for the wire Sn-9-'30, in which the tetragonal axis made an angle of  $45^\circ$  with the axis of the wire.

Here too the magnetic transition figure always had the same character.

Though only few data have been collected as yet, we get the impression, that the character of the magnetic transition figure is independent of the orientation of the crystal axis with respect to the axis of the wire.

Here again our opinion is supported by comparison with the magnetic transition curves of polycrystalline tin wires.

So our experiments have revealed many new phenomena. Still a refinement and an extension of them is desirable. In our opinion the principal point found is the characteristic difference between the longitudinal and the transverse disturbance.

In further experiments we shall try to learn something more of the mechanism of the magnetic disturbance (both longitudinal and transverse) in the wire. Hence we must find out how far in the different stages of the magnetic transition curves the magnetic field has intruded into the wire.

#### § 5. *Influence of the temperature on the magnetic disturbance.*

In order to find the dependance of the magnetic disturbance on the temperature, we considered in our earlier researches at different temperatures the intensity of the field in which the resistance had regained half its normal value. For one and the same temperature this magnetic half-value was found to be always higher for the longitudinal disturbance than for the transverse disturbance. Then the hysteresis phenomenon had not yet been found, though all these measurements were made with poly-crystalline wires (The hysteresis of these must have been very small).

Now that the hysteresis had been found the magnetic half value has lost its meaning, so that a new agreement had to be made as to the way in which the influence of the temperature could be indicated.

A very characteristic field intensity, perfectly reproducible, is that for which in a longitudinal field the resistance of a single-crystalline wire comes back. This restoration is so sharply defined that it can hardly be discerned between the point where the resistance begins to come back and that in which it has regained its normal value.

For poly-crystalline wires the case is different. Here the transition curve is not sharp. That is why we must take here the magnetic half value for the rising curve of the longitudinal disturbance as a characteristic field intensity.

In fig. 3 we have plotted for single-crystalline wires the temperature as a function of the field intensity for which in a longitudinal and in a transverse magnetic field the resistance begins to come back.

The values in the figure are the mean of those found for different single-crystalline wires, which differed very little from each other. It is seen that in a longitudinal field the resistance comes back in about the same field in

which in a transverse magnetic field the resistance has just regained its normal value.

Further the magnetic range in which the resistance comes back in the transverse case, is seen to be proportional to the intensity of the field in which the resistance is totally restored.

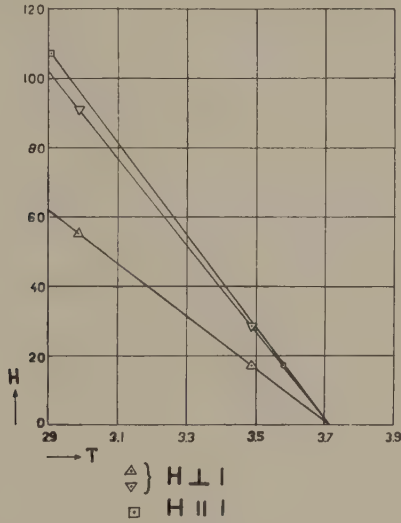


Fig. 3.

From the figure it is also evident, that for the transverse disturbance the magnetic half value of the rising curve will be smaller than for the longitudinal disturbance, which has always been observed in the case of polycrystalline wires with small hysteresis.

We wish to express our thanks to Mr. P. M. VAN ALPHEN for his valuable help during the experimentation.

**Physics.** — *The change in resistance of graphite, thorium, titanium, titanium-zirconium between 20°.4 K. and 1°.1 K.* By W. J. DE HAAS and P. M. VAN ALPHEN. (Communication N°. 212e from the Physical Laboratory Leiden.)

(Communicated at the meeting of January 31, 1931).

### § 1. Graphite.

The typical behaviour of good graphite crystals at low temperatures induced us to investigate the change of their resistance at the temperature of liquid hydrogen and helium.

We prepared several resistances from a well crystallized block of Ceylon graphite; so that the crystalline state of our resistances was probably homogeneous. The rods were about 15 mm long; their extremities were coated with copper, to which the current and potential wires could be soldered. The principal axis is perpendicular to the longitudinal direction, in which direction the current flows.

For different samples we measured the resistance changes which were found to be very great. We then selected those resistances for which this change amounted to 300 % in a field of 15 kg and of these selected samples we determined the resistance at 14°.2. Finally the crystal with the lowest value of  $R/R_0$  was examined in liquid helium.

TABLE I.

$p \text{ He}$	$T$	$R/R_0$
	20.43°	0.2138
	17.14	0.1840
	11.36	0.1377
776.53	4.25	0.1219
398.42	3.58	0.1209
93.31	2.59	0.1199
24.07	2.03	0.1196
4.74	1.52	0.1194
0.58	1.15	0.1193

1) D. E. ROBERTS, Ann. d. Phys. 40, 453, 1913.

It is seen, that the resistance in a direction perpendicular to the principal axis changes very little in the helium region. The residual resistance agrees

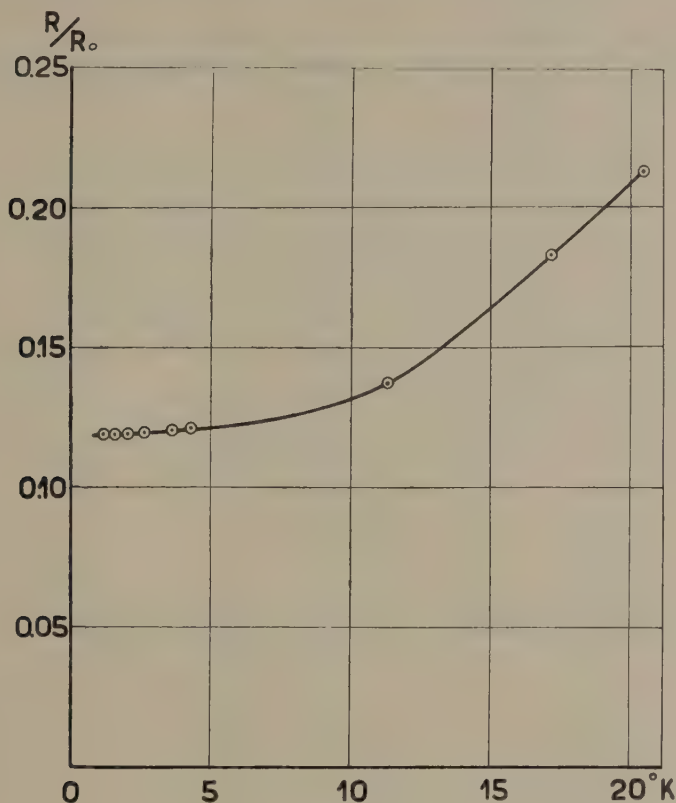


Fig. 1.

approximately with that found in earlier experiments for purified and compressed graphite powder <sup>1)</sup>.

## § 2. Thorium.

Thorium, titanium and titanium-zirconium were all used as crystals precipitated from the gaseous states.

They were all prepared by Dr. G. DE BOER from the PHILIPS works Eindhoven, to whom we gladly express our thanks for his valuable help.

The thorium crystal was very short and rather thick, so that the resistance was small. The current was lead trough german silver clamps.

Part of the same crystal had been investigated by Dr. W. MEISSNER, Berlin ; it was found to become supraconducting at  $1^{\circ}.4$  <sup>2)</sup>.

<sup>1)</sup> H. KAMERLINGH ONNES and K. HOF, Proc. Roy. Ac. Amsterdam, **17**, 520, 1915. Comm. Leiden, N<sup>o</sup>. 142b.

<sup>2)</sup> W. MEISSNER, Naturwiss. **17**, 390, 1929; Z. f. Phys. **61**, 191, 1930.



TABLE II.

$p\text{ He}$	$T$	$R/R_0$
763.52	4.22°	0.0170
23.97	2.00	0.0163
17.47	1.89	0.0163
9.46	1.70	0.0042
7.54	1.64	0.0024
5.82	1.57	0.0013
4.69	1.52	0.0004
2.68	1.40	supra
1.43	1.29	"
0.58	1.15	"

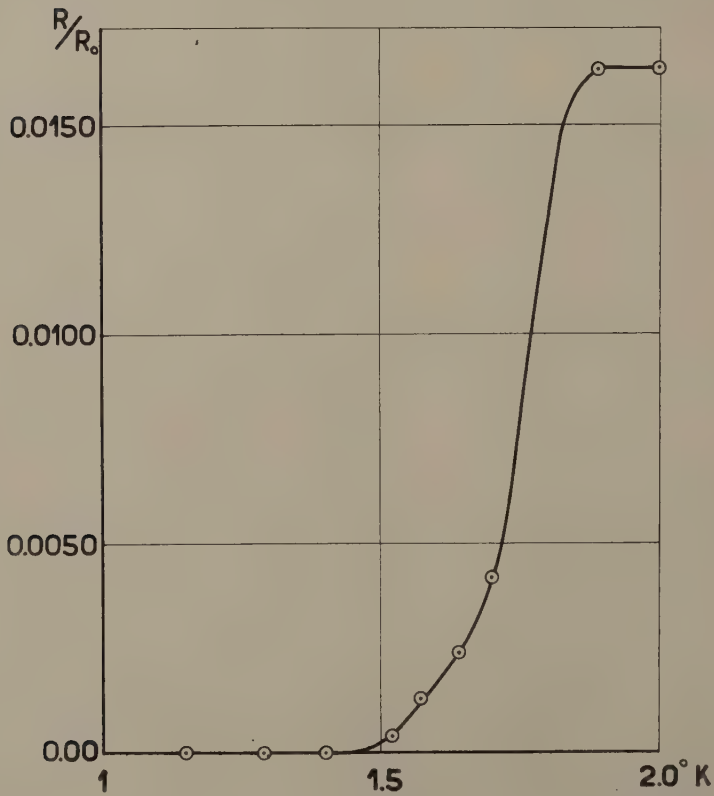


Fig. 2.

The part examined by us keeps its normal resistance down to  $1^{\circ}.9$ ; here the resistance begins to decrease and has become zero at  $1^{\circ}.4$ . The vanishing covers a range of  $0^{\circ}.5$ , which is very much for a single-crystal.

The differences with the measurements of Dr. MEISSNER are considerable, so that probably the crystal is rather impure and perhaps is really not a single-crystal.

### § 3. *Titanium and the mixed crystal titanium-zirconium*<sup>1)</sup>.

Here too the extremities of the crystals were coated with copper and the current and potential wires were soldered to this.

The resistance of the titanium falls from  $1^{\circ}.88$  to  $1^{\circ}.63$ , that of the titanium-zirconium from  $1^{\circ}.63$  to  $1^{\circ}.12$ .

Dr. MEISSNER found for titanium a steep fall at  $1^{\circ}.2$  (from 0.5—1.5 mm Hg)<sup>2)</sup>.

With another rod he found a higher transition point<sup>3)</sup>. In the first case the value of  $R/R_0$  at  $4^{\circ}.2$  was 0.215, viz. nearly twice that found by us.

Zirconium does not become supraconducting<sup>4)</sup>.

TABLE III.

$p\text{ He}$	$T$	$R/R_0$ Titan	$R/R_0$ Titan. zircon.
	20.41	0.1051	0.1978
	18.06		0.1961
	16.21		0.1952
	14.25		0.1946
761.57	4.22	0.1048	0.1934
24.67	2.01	0.1047	0.1934
17.11	1.88	0.1018	
12.44	1.78	0.0433	
10.38	1.73	0.0011	
7.37	1.63	supra	0.1916
2.56	1.39	..	0.0792
1.71	1.32	..	0.0361
0.45	1.12	..	supra

<sup>1)</sup> J. H. DE BOER and P. CLAUSING, *Physica* **10**, 267, 1930.

<sup>2)</sup> W. MEISSNER, *Z. f. Phys.* **60**, 181, 1930.

<sup>3)</sup> W. J. DE HAAS and J. VOOGD, *Comm. Leiden* N<sup>o</sup>. 194c.

<sup>4)</sup> W. MEISSNER, *Ann. d. Phys.* **7**, 894, 1930.

The purity of these metals seems to be not so great that reproducible data can be obtained.

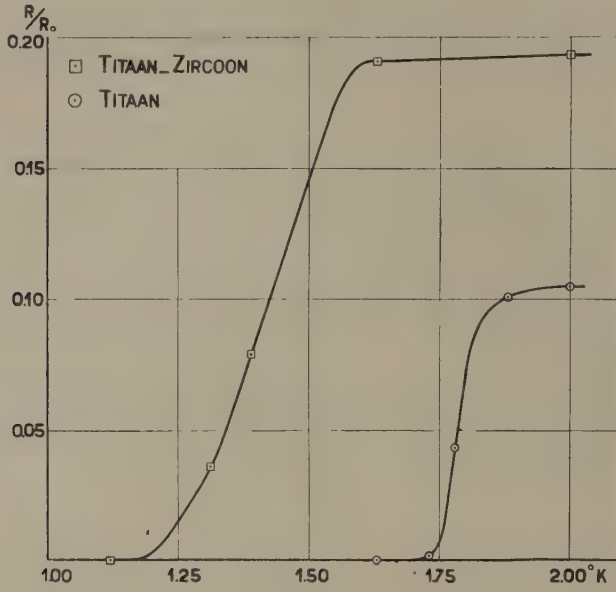


Fig. 3.

**Physics.** — *Thermal conductivity of tin at low temperature.* By W. J. DE HAAS, S. AYOAMA and H. BREMMER. (Communication No. 214a from the Physical Laboratory Leiden.)

(Communicated at the meeting of January 31, 1931).

§ 1. *Introduction and method.* The sample of tin we examined was a small rod of pure tin from KAHLBAUM 9 cm long and 1.8 mm thick.

The measuring method was in principle the same as that used first by LEES <sup>1)</sup>. Afterwards it was used by many others in a somewhat modified form, e.g. recently by GRÜNEISEN and GOENS at low temperatures <sup>2)</sup>.

The rod to be investigated is mounted in a metal cylinder which can be evacuated. The lower extremity of the rod is fixed to the bottom of the cylinder and takes the temperature of the vessel while a known quantity of energy is electrically conducted to its upper extremity. To determine the thermal conductivity the temperature of the rod had to be measured at two places. GRÜNEISEN and GOENS did this by means of thermo-elements. We followed a different way, which may be sketched here preliminarily only, as we will soon communicate the complete description of the apparatus. The temperature of the upper end of the rod was determined with a gas thermometer, while the lower end as has been mentioned had the temperature of the metal cylinder. The extremities were soldered with the same tin from which they were prepared to the metallic gas thermometer and to the bottom of the vessel respectively. The vessel was placed in liquid hydrogen or oxygen the temperatures of which were determined with a platinum resistance thermometer.

As was done also by other investigators the energy was supplied electrically viz. by a constantan wire of about 300  $\Omega$  resistance which was wound in a special way and connected to the bottom of the gas thermometer. Corrections for the loss and gain of energy by radiation and convection as far as not due to the tin rod, were determined by a separate experiment, in which the tin rod was taken away of course.

The gas thermometer was filled with helium; its sensitivity was regulated by choosing for each experiment a suitable zero pressure. Before each measurement (before the energy was supplied to the rod) the gas thermometer was compared with the platinum resistance thermometer. For this calibration heliumgas was admitted in the metal vessel in order

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<sup>1)</sup> Phil. Trans. 208, 381, 1908.

<sup>2)</sup> Z. f. Phys. 44, 615, 1927.

to secure good thermal contact between the bulb of the gas thermometer and the bath of the liquid.

§ 2. *The temperatures.* As will be known the hydrogen temperatures range from  $12^\circ$  K (solid hydrogen) to  $20^\circ$  K (boiling point under normal pressure), the oxygen temperatures from  $76^\circ$  K (boiling point under 13 cm pressure) to  $90^\circ$  K (boiling point under 76 cm).

Our apparatus however enabled us to bridge the gap between these two temperature intervals. We had only to supply more energy and to increase the temperature gradient in the rod.

Let  $T_0$  be the temperature of the bath (in this case the boiling point of hydrogen under normal pressure),  $T_1$  the temperature of the gas thermometer,  $i$  the energy supplied electrically per second,  $w(T)$  the thermal resistance the rod would have if it had the same temperature over its whole length.

We then have:

$$i = \int_{T_0}^{T_1} \frac{dT}{w(T)}$$

If  $T_1$  is taken successively for two neighbouring values  $T_a$  and  $T_b$ , to which in stationary state the energy currents  $i_a$  and  $i_b$  belong, we can write:

$$i_a - i_b = \int_{T_b}^{T_a} \frac{dT}{w(T)}.$$

If  $T_a - T_b$  is small, this gives the thermal resistance for the mean temperature between  $T_a$  and  $T_b$ .

We may assume namely that between  $T_a$  and  $T_b$   $w(T)$  is a linear function of  $T$ , which assumption is also made for measurements in the hydrogen and oxygen regions. Here too it is allowed with a view to the accuracy of 1%.

For the points between the hydrogen and oxygen temperatures, however, we must know the difference of two energy currents. That is why in this interval the accuracy is less.

§ 3. *Results.* In the table 1 we give the values  $w$  determined by measurements for the thermal resistance of the rod (unit Watt<sup>-1</sup>). We cannot derive from these with sufficient accuracy the coefficient of thermal conduction in absolute terms because of the indefinite form of the contact places at the extremities of the rod.



TABLE 1.

$T$	$W$	$T$	$W$
12.5	110	34.8	288
14.8	120	54	371
15.4	130	76	433
20.7	174	97	470
22.9	194		

In fig. 1 the  $T$ — $W$  curve has been plotted. The form of this curve is essentially the same as that found by GRÜNEISEN and GOENS in their

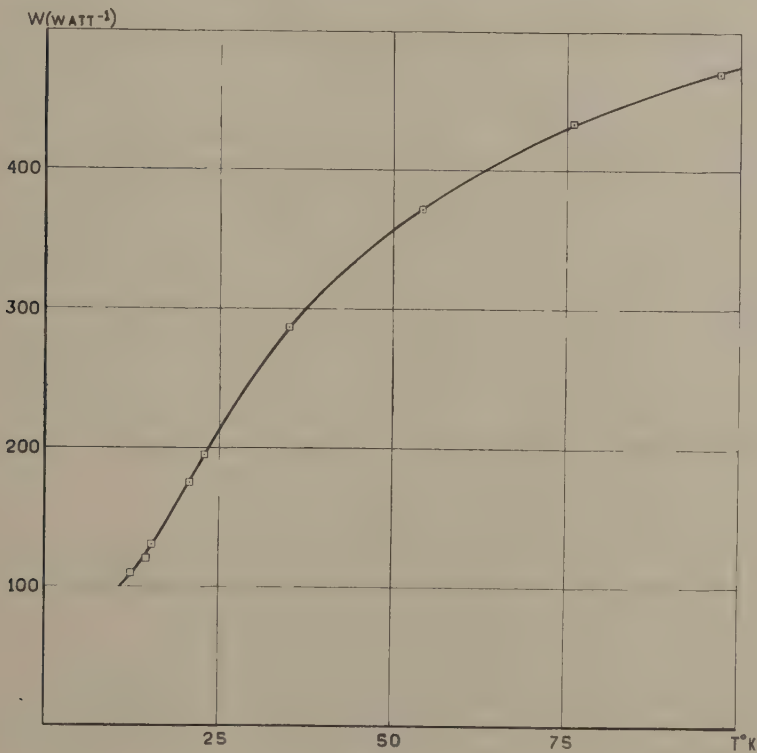


Fig. 1.

researches on pure metals at low temperatures. Both our curve and theirs show a point of inflection.

**Chemistry.** — *Osmosis in systems in which also liquids with constant composition.* II. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of January 31, 1931).

*The curve of the stational liquids.*

If we leave the osmotic systems :

$$\text{inv. } L(1) \mid L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$L \mid \text{inv. } L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

to themselves, then the variable liquid  $L$  will change its composition ; in system (1)  $L$  will at last become equal to  $L(1)$  and in system (2) equal to  $L(2)$ ; in both systems the osmosis will then be ended <sup>1)</sup>.

In the osmotic system

$$\text{inv. } L(1) \mid L \mid \text{inv. } L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

however, the variable liquid  $L$  is found between the two invariable liquids  $L(1)$  and  $L(2)$ ; if we now leave this system to itself, the variable liquid will at last get a constant composition ; it is clear, however, that  $L$  does not become equal to  $L(1)$  now, as in system (1), neither does it get equal to  $L(2)$  as in system (2); we shall call this liquid which arises spontaneously during the osmosis and which remains constant of its own accord a "stational" liquid <sup>2)</sup>. So system (3) passes spontaneously into a system. which we shall represent by :

$$\text{inv. } L(1) \mid \text{stat. } L \mid \text{inv. } L(2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the stational liquid has a definite composition.

In systems (1) and (2) the osmosis will be ended when the variable liquid has got the same composition as the invariable one. However, when system (3) has passed into system (4), the osmosis is not done ; this is clear because the three liquids then keep different compositions all the time and nor can they possibly ever become equal to one another. Consequently system (4) does not represent a state of equilibrium, but a stationary state, in which osmosis still goes on all time ; here the stational liquid only changes its quantity, however, but not its composition. Later on we shall discuss some experimentally determined examples of similar systems.

<sup>1)</sup> F. A. H. SCHREINEMAKERS. These Proceedings **33**, 344 (1930).

<sup>2)</sup> i.e.

Above we have said that the stationary liquid  $L$  of system (4) has a definite composition; this depends, however, as we shall see later on, upon the nature of the two membranes and the ratio of their surfaces. For this reason we now imagine in system (3) two definite membranes  $M_1$  and  $M_2$  with the surface  $\omega_1$  and  $\omega_2$ ; we represent this by:

$$\text{inv. } L(1) \left| \begin{array}{c} M_1 \\ \omega_1 \end{array} \right| L \left| \begin{array}{c} M_2 \\ \omega_2 \end{array} \right| \text{inv. } L(2) \dots \dots \dots (5)$$

If we leave this system to itself, then at last the stationary system:

$$\text{inv. } L(1) \left| \begin{array}{c} M_1 \\ \omega_1 \end{array} \right| \text{stat. } L \left| \begin{array}{c} M_2 \\ \omega_2 \end{array} \right| \text{inv. } L(2) \dots \dots \dots (6)$$

will arise, in which the composition of the stationary liquid  $L$  is determined by the nature of the membranes  $M_1$  and  $M_2$  and the ratio  $\omega_1 : \omega_2$  of their surfaces.

Now we imagine the invariable liquids  $L(1)$  and  $L(2)$  and the stationary liquid  $L$  in fig. 1 represented by the points 1, 2 and  $u$ ; we shall call  $u$  a stationary point.

With every change of the nature of one of the membranes and with every change of the ratio  $\omega_1 : \omega_2$  of their surfaces, the stationary liquid  $L$  of system (6) gets an other constant composition and the stationary point  $u$  in fig. 1 an other place. If we only change the ratio  $\omega_1 : \omega_2$  then the stationary liquid moves along a curve 1  $u$  2 (fig. 1) which we shall call the "curve of stationary liquids".

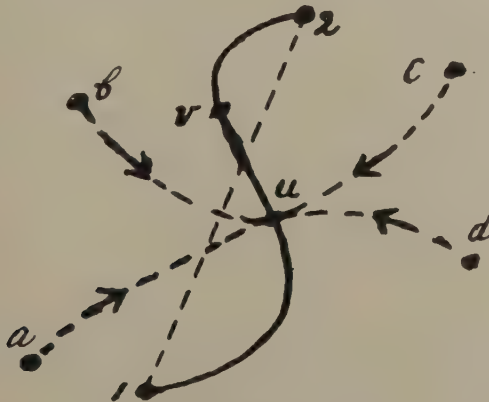


Fig. 1.

It is easy to see that this curve must go through the points 1 and 2. If namely we take the surface  $\omega_1$  of the membrane  $M_1$  very small, then it is clear that also a small quantity only will be able to diffuse through this membrane; in the limit-case  $\omega_1 = 0$  nothing will diffuse any more either towards or from liquid  $L(1)$  so that we may as well omit this;

then system (6) passes into system (2), in which the liquid  $L$  gets the same composition as the invariable liquid  $L(2)$ .

If we take  $\omega_2 = 0$ , system (6) passes into system (1) so that  $L$  gets the same composition as  $L(1)$ . From this appears:

for small values of  $\omega_1$  the stational liquid of system (6) is situated close to point 2 and for small values of  $\omega_2$  close to point 1 (fig. 1).

It also follows from these considerations:

the form of the curve of stational liquids of system (6) only depends upon the nature of the two membranes  $M_1$  and  $M_2$ ;

the place of the stational liquid on this curve only depends upon the ratio  $\omega_1 : \omega_2$  of the surface of these membranes.

### *The up to a stational liquid path.*

We now imagine the variable liquid  $L$  of the systems (1), (2) and (5) represented by point  $a$  of fig. 1.

During the osmosis in system (1) this variable liquid proceeds along a path, not drawn in the figure, starting from  $a$  and terminating in point 1. Formerly<sup>1)</sup> we have called this path  $a1$  the "up to inv.  $L(1)$  path" of liquid  $a$ .

In system (2) the variable liquid proceeds during the osmosis along a path  $a2$ , not drawn in the figure, viz. the up to inv.  $L(2)$  path of liquid  $a$ .

In system (5) the variable liquid also proceeds during the osmosis along a path starting from  $a$ ; this does not terminate however either in point 1 or in point 2, but in a point representing the stational liquid of system (6), e.g. in point  $u$ . We shall call this path  $au$  the "up to stat.  $L(u)$  path" of liquid  $a$ .

When the variable liquid has come in the final point  $u$  of its path, then, as we have discussed already above, the osmosis is not done, but a stationary state obtains; henceforth the stational liquid will only change its quantity and not its composition any more.

As we may take any liquid for  $L$  in system (5), an infinite number of up to stat.  $L(u)$  paths will of course exist; in fig. 1 the paths starting from the points  $a$ ,  $b$ ,  $c$  and  $d$  have been drawn.

Above we have assumed that all up paths end in point  $u$ . Of course this is only the case when  $\omega_1 : \omega_2$  in system (5) has a definite value. If we change this ratio, then the final point will also come in an other place e.g. in point  $v$ ; then the liquid proceeds along a curve  $av$  or  $bv$  etc. which we shall call an up to stat.  $L(v)$  path.

As this final point may be situated anywhere on the curve  $1u2$ , each liquid, therefore, may proceed along an infinite number of paths; we can call them the "up to a stational liquid paths" of this liquid. As has been

<sup>1)</sup> l.c.

said already above, it depends upon the ratio  $\omega_1 : \omega_2$  along which of these paths a liquid will travel.

In order to illustrate the preceding considerations, we take the stationary system :

$$\overset{M_1}{\text{inv. } L(1)} \mid \overset{M_2}{\text{stat. } L(z)} \mid \text{inv. } L(2) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$\omega_1 \qquad \qquad \qquad \omega_2$

This represents a stationary state in which the osmosis is not done, but is still going on all the time. We now shall distinguish two diffusing mixtures viz.  $D(1)$  which diffuses through the membrane  $M_1$  and  $D(2)$  which diffuses through the membrane  $M_2$ ; we represent by  $\delta m_1$  and  $\delta m_2$  the quantities of these mixtures diffusing in the time  $\delta t$ . We take these quantities positive, when they are absorbed by  $L(z)$ , negative, when they are given off by  $L(z)$ . So the liquid  $L(z)$  absorbs in the time  $\delta t$  :

$$\delta m_1 \text{ quant. } D(1) + \delta m_2 \text{ quant. } D(2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We may also say now that  $L(z)$  absorbs  $\delta m_1 + \delta m_2$  quantities of a mixture which we shall call  $D$ . As we assume, however, that during the osmosis  $L(z)$  does not change its composition, this mixture  $D$  must have the same composition as  $L(z)$ ; consequently we must have :

$$\delta m_1 \times D(1) + \delta m_2 \times D(2) = (\delta m_1 + \delta m_2) \times L(z) \quad . \quad . \quad (9)$$

in which, as has been said already above,  $\delta m_1$  and  $\delta m_2$  can be positive as well as negative.

We now represent in fig. 2 the liquids  $L(1)$ ,  $L(2)$  and  $L(z)$  of system (7) by the points 1, 2 and  $z$ ; we suppose the diffusing mixtures  $D(1)$  and  $D(2)$  to be represented by the points  $D(1)$  and  $D(2)$ , which have not been drawn. It follows from (9) that the points  $D(1)$ ,  $D(2)$  and  $z$  must be situated on a straight line; in fig. 2 we represent this by  $p_1 z p_2$ .

So we find as primary condition for the existence of the stationary liquid  $L(z)$  :

a. the stationary liquid  $L(z)$  and the two diffusing mixtures  $D(1)$  and  $D(2)$  must in the graphical representation be situated on a straight line.

If we represent by  $k_1$  and  $k_2$  the quantities of  $D(1)$  and  $D(2)$ , diffusing every second through 1 cm<sup>3</sup> of the membranes  $M_1$  and  $M_2$ , we have :

$$\delta m_1 = \omega_1 K_1 \delta t \qquad \delta m_2 = \omega_2 K_2 \delta t \quad . \quad . \quad . \quad . \quad (10)$$

In accordance with the above we take  $k_1$  and  $k_2$  positive when  $D(1)$  and  $D(2)$  are absorbed by the liquid  $z$ ; negative when these mixtures are given off by the liquid  $z$ .

If we substitute these values in (9) and if we divide by  $\delta t$ , we find :

$$\omega_1 K_1 \times D(1) + \omega_2 K_2 \times D(2) = (\omega_1 K_1 + \omega_2 K_2) \times L(z) \quad . \quad (11)$$

From this we find :

$$\frac{L(z) - D(2)}{D(1) - L(z)} = \frac{K_1}{K_2} \cdot \frac{\omega_1}{\omega_2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$



From this it appears that condition (a) mentioned above, is not sufficient to produce the stationary state; it appears namely from (12):

b. the stationary liquid  $L(z)$  and the two diffusing mixtures  $D(1)$  and  $D(2)$  have besides to satisfy a condition, in which the ratio  $\omega_1 : \omega_2$  of the membranes plays a part.

We now represent the composition of  $L(z)$  by:

$$x \text{ mol } X + y \text{ mol } Y + (1-x-y) \text{ mol } W \quad . \quad . \quad . \quad (13)$$

and that of the diffusing mixtures  $D(1)$  and  $D(2)$  by:

$$\left. \begin{aligned} x_1 \text{ mol } X + y_1 \text{ mol } Y + (1-x_1-y_1) \text{ mol } W \\ x_2 \text{ mol } X + y_2 \text{ mol } Y + (1-x_2-y_2) \text{ mol } W \end{aligned} \right\} \quad . \quad . \quad . \quad (14)$$

As we have seen previously<sup>1)</sup>  $x_1$ ,  $y_1$ ,  $x_2$  and  $y_2$  may here be positive as well as negative. [Of course this is not the case with  $x$  and  $y$  in (13).] It now follows from (11):

$$\left. \begin{aligned} x_1 \omega_1 K_1 + x_2 \omega_2 K_2 &= (\omega_1 K_1 + \omega_2 K_2) x \\ y_1 \omega_1 K_1 + y_2 \omega_2 K_2 &= (\omega_1 K_1 + \omega_2 K_2) y \end{aligned} \right\} \quad . \quad . \quad . \quad (15)$$

which we also may write in the form:

$$\left. \begin{aligned} (x_1-x) \omega_1 K_1 + (x_2-x) \omega_2 K_2 &= 0 \\ (y_1-y) \omega_1 K_1 + (y_2-y) \omega_2 K_2 &= 0 \end{aligned} \right\} \quad . \quad . \quad . \quad (16)$$

From this follows:

$$\frac{K_2}{K_1} \cdot \frac{x_2-x}{x_1-x} = -\frac{\omega_1}{\omega_2} \quad \text{and} \quad \frac{K_2}{K_1} \cdot \frac{y_2-y}{y_1-y} = -\frac{\omega_1}{\omega_2} \quad . \quad . \quad . \quad (17)$$

We now first take the equation, following from this:

$$\frac{y_1-y}{x_1-x} = \frac{y_2-y}{x_2-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If we suppose  $x$  and  $y$  are variables here, then (18) represents a straight line, going through point  $x_1 y_1$  [viz.  $D(1)$ ] and point  $x_2 y_2$  [viz.  $D(2)$ ]. From this it follows, as has already been stated above in a, that the points  $z$ ,  $D(1)$  and  $D(2)$  must be situated on a straight line.

Of course the composition  $x_1 y_1$  of the diffusing mixture  $D(1)$  and the quantity  $K_1$ , diffusing per second through 1 cm<sup>3</sup> of the membrane  $M_1$ , depend upon the composition of the invariable liquid  $L(1)$ , on the composition  $x y$  of the liquid  $L(z)$  and on the nature of the membrane  $M_1$ . Consequently we have:

$$x_1 = \varphi_1(xy) \quad y_1 = \psi_1(xy) \quad K_1 = Z_1(xy) \quad . \quad . \quad (19)$$

<sup>1)</sup> F. A. H. SCHREINEMAKERS. Deze Verslagen 36, 1103 (1927).

These Proceedings 30, 1095 (1927).

in which the functions  $\varphi_1$ ,  $\psi_1$  and  $Z_1$  contain not only  $x$  and  $y$ , but the composition of liquid  $L(1)$  besides and the magnitudes determining the behaviour of the membrane  $M_1$ .

We now put also :

$$x_2 = \varphi_2(xy) \quad y_2 = \psi_2(xy) \quad K_2 = Z_2(xy) \quad . \quad . \quad (20)$$

Besides  $x$  and  $y$  these functions contain also the composition of liquid  $L(2)$  and the magnitudes, determining the behaviour of the membrane  $M_2$ .

If we substitute (19) and (20) in (17), we see that we may write instead :

$$f(xy) = -\frac{\omega_1}{\omega_2} \quad F(xy) = -\frac{\omega_1}{\omega_2} \left\{ . \quad . \quad . \quad . \quad . \quad . \quad (21) \right.$$

in which the functions  $f$  and  $F$  contain not only  $x$  and  $y$ , but also the compositions of the liquids  $L(1)$  and  $L(2)$  and the magnitudes determining the behaviour of each of the membranes  $M_1$  and  $M_2$ .

Consequently we have two equations between  $x$ ,  $y$  and  $\omega_1 : \omega_2$ . If we leave unchanged the compositions of the liquids  $L(1)$  and  $L(2)$  and the nature of the membranes  $M_1$  and  $M_2$ , then it appears that to each value of  $\omega_1 : \omega_2$  belongs also a definite value of  $x$  and  $y$ ; this means: in system (7) a definite composition of the stational liquid  $L(z)$  belongs to each value of  $\omega_1 : \omega_2$  and a definite position of point  $z$  in fig. 2. This is in accordance with what we have said above in *b*.

From this it follows also: if we change the ratio  $\omega_1 : \omega_2$ , the stational liquid  $L(z)$  of system (7) proceeds along a curve, which has been determined by :

$$f(xy) = F(xy). \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

We have called this curve the curve of the stational liquid and have represented it in fig. 1 by curve 1 *uv* 2. It appears from (22) that the shape of this curve depends only upon the compositions of the liquids  $L(1)$  and  $L(2)$  and on the nature of the membranes  $M_1$  and  $M_2$ .

If in system (7) we close up membrane  $M_2$ ,  $L(z)$  cannot remain constant any longer; at last it will become equal to  $L(1)$ . Then the liquid proceeds along its up to inv.  $L(1)$  path, which has been represented in fig. 2 by curve  $z1$ . When  $zp_1$  is the tangent in point  $z$  of this path  $z1$ , the liquid  $z$  moves an infinite small distance along this tangent during the first moment in the direction from  $z$  towards  $p_1$ ; the mixture  $D(1)$  diffusing at this moment is situated then, as we have seen previously<sup>1)</sup>, somewhere on this tangent  $zp_1$  (or on its prolongation).

If we close up membrane  $M_1$ , then the liquid proceeds along its up to inv.  $L(2)$  path, which has been represented in fig. 2 by  $z2$ . When  $zp_2$  is the tangent in point  $z$  of this path  $z2$ , then the liquid moves an infinite

<sup>1)</sup> l.c.

small distance along this tangent during the first moment in the direction from  $z$  towards  $p_2$ . The mixture  $D(2)$  diffusing at this moment is then situated somewhere on this tangent  $zp_2$  (or on its prolongation).

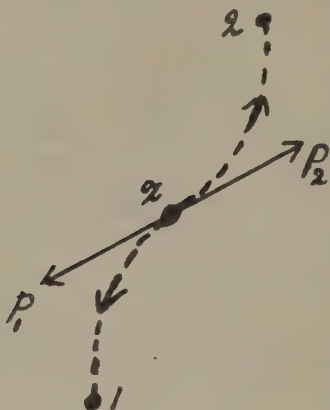


Fig. 2.

So in system (7) in which both membranes are open, two influences (viz. the diffusion through the membranes  $M_1$  and  $M_2$ ) affect liquid  $z$ ; one tries to move it from  $z$  towards  $p_1$  in fig. 2, the other from  $z$  towards  $p_2$ . It is clear that this liquid can only remain in point  $z$  when two conditions have been satisfied.

A) The tangents  $zp_1$  and  $zp_2$  must be situated in each other's prolongation. This is in accordance with what we have seen already above in *a*, namely that the points  $D(1)$ ,  $D(2)$  and  $z$  must be situated on a

straight line. We now may say also: the up to inv.  $L(1)$  path  $z1$  and the up to inv.  $L(2)$  path  $z2$  must touch one another in point  $z$ .

B) Liquid  $z$  moves towards  $p_1$  under one influence, towards  $p_2$  under the other; it can remain in its place only then when these shiftings, which of course depend also upon the surfaces  $\omega_1$  and  $\omega_2$  of the two membranes, are the same at any moment. From this follows, what has already been said previously in *b*, that there must be a connection between the compositions of  $L(z)$ ,  $D(1)$  and  $D(2)$  and the ratio  $\omega_1 : \omega_2$  of the surfaces of the membranes. If we calculate these shiftings, we are able to find the relations (12) and (17) in this way.

Above we have already pointed out several times that the quantity of the stationary liquid  $L(z)$  changes continuously during the osmosis. When  $L(z)$  takes in the two diffusing mixtures, its quantity increases continuously; when  $L(z)$  gives off these mixtures, its quantity decreases; when  $L(z)$  takes in the one mixture, but gives off the other, then the quantity may increase or decrease. In the one case more and more liquid gathers all the time between the two invariable liquids; in the other case this liquid will disappear. Later on we shall discuss these conditions more in detail.

These phenomena may occur also when the two invariable liquids do not surround one, but a whole series of liquids, connected by membranes; then we have systems, resembling vegetable and animal tissues; we shall refer to this later on.

(To be continued.)

Leiden, Lab. of Inorganic Chemistry.

**Chemistry.**— IV. *The Exact Measurement of the Specific Heat of Osmium and Rhodium between 0° and 1625° C.* By F. M. JAEGER and E. ROSENBOHM.

(Communicated at the meeting of January 31, 1931).

§ 1. In this paper the results are communicated, which have been obtained in the exact measurement of the variation of the specific heats of *osmium* and *rhodium* with the temperature, within the interval of 0° and 1625° C. The measurements were executed with all care and with the precautions formerly mentioned<sup>1)</sup>. The method followed was the one previously described. By controlling experiments and repeated determinations of the different points of the curves in arbitrarily chosen sequence, it was ascertained that the results really were perfectly reproducible within less than one tenth of a percent, — even at the highest temperatures considered. We wish to express once more our thanks to the firm of Dr. W. C. HERAEUS in *Hanau*, which most courteously put greater quantities of the purest metals at our disposal and which with great care and ability, gave us its assistance in the preliminary preparation of the materials used in this investigation. Also during these measurements it once more appeared, that the most serious source of error present was the occasional contamination of the thermocouples, — especially at higher temperatures. For this reason the reliability of the thermoelement-readings was more particularly considered and the thermoelements repeatedly tested, while all precautions were taken to prevent such contamination as well as possible.

§ 2. I. By a special method it was attained to enclose 28,0645 grammes of purest *osmium*, in the shape of pea-sized globulets, within the evacuated platinum vessels of the form previously described<sup>2)</sup>, without any oxidation of the metal having occurred. In Table I the results of the measurements are collected.

From these data it can be concluded, that the amount of heat  $Q'_0$  given off by 1 gramme of the metal between  $t^\circ$  and 0° C., can very accurately be represented by the formula :

$$Q'_0 = 0,030986 \cdot t + 0,0000023606 \cdot t^2.$$

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<sup>1)</sup> F. M. JAEGER and E. ROSENBOHM, *Recueil des Trav. Chim. d. Pays-Bas*, **47**, (1928), 513; these *Proceed.*, **33**, (1930), 457.

TABLE I. Specific Heats of Osmium between 0° and 1625° C.

Temperature $t$ in Cent.:	Final tempe- rature $t'$ of Calorimeter:	Increase of temperature $\Delta t$ of Calorimeter:	Weight of Osmium:	Weight of Platinum:	Mean specific Heat $c_p$ of Osmium be- tween $t$ and $t'$ :	Total Amount of Heat given off by 1 Gr. between $t$ and $t'$ (calories):	Total Amount Q of Heat de- livered between $t'$ and 0° by 1 Gr. (calories):	Total Amount of Heat $Q_0$ de- livered between $t$ and 0° by 1 Gr. (in calories):	Total Amount $Q'_0$ of Heat delivered between $t$ and 0°, as calculated from the formula:
419.4	20.599	0.52369	28.0645	27.286	0.03047	12.777	0.638	13.415	13.411
630.1	20.923	0.81590	28.0645	27.291	0.03141	19.794	0.649	20.443	20.461
800.8	21.260	1.0551	28.0645	27.294	0.03205	25.651	} 0.656	26.310	} 26.326
800.8	21.061	1.0557	28.0645	27.285		25.686		26.339	
999.8	21.570	1.3446	28.0645	27.285	0.03265	32.646	0.668	33.314	33.319
1201.9	21.795	1.6493	28.0645	27.285	0.03324	39.949	0.674	40.623	40.646
1391.6	21.959	1.9454	28.0645	27.294	0.03378	47.011	0.680	47.691	47.691
1391.2	21.949	1.9460	28.0645	27.326	0.03378	46.996	0.680	47.676	47.686
1539.6	22.681	2.1960	28.0645	27.388	0.03417	52.610	0.703	53.313	53.302
1603.7	22.594	2.2898	27.6163	27.448	0.03484	55.082	0.700	55.782	55.766



The specific heat under constant pressure  $c_p$  can, therefore, be calculated from the linear equation :

$$c_p = \frac{dQ'_0}{dt} = 0,030986 + 0,000004721 \cdot t.$$

The dependency of  $c_p$  on  $t$  is, therefore, practically a linear one ; the specific heat at  $0^\circ \text{C.}$ , by extrapolation, can be calculated at :

$$c_p^{0^\circ} = 0.030986.$$

A direct determination of  $c_p$  with the aid of a supplementary calorimeter gave a value of : 0,0320 at  $0^\circ \text{C.}$ , with an uncertainty of about 1 %.

In the following table the values of  $c_p$  and of the atomic heat  $C_p$  of osmium are given for a series of temperatures between  $0^\circ$  and  $1600^\circ \text{C.}$

Specific and Atomic Heats under Constant Pressure of Osmium at different Temperatures.		
Temperature in $^\circ \text{C.}$ :	Specific Heat $c_p$ :	Atomic Heat $C_p$
$0^\circ$	0.03099	5.915
$100^\circ$	0.03146	6.006
$200^\circ$	0.03193	6.096
$300^\circ$	0.03240	6.185
$400^\circ$	0.03287	6.276
$500^\circ$	0.03335	6.367
$600^\circ$	0.03382	6.455
$700^\circ$	0.03429	6.546
$800^\circ$	0.03476	6.636
$900^\circ$	0.03503	6.687
$1000^\circ$	0.03571	6.817
$1100^\circ$	0.03618	6.907
$1200^\circ$	0.03665	6.996
$1300^\circ$	0.03712	7.086
$1400^\circ$	0.03759	7.176
$1500^\circ$	0.03807	7.268
$1600^\circ$	0.03854	7.358

The atomic heat  $C_p$  can be expressed fairly well by :

$$C_p = 5,9152 + 0,0009019 \cdot t.$$

As in literature all data about the thermal dilatation and the compressibility of *osmium* are lacking, it is impossible even to give only an approximate estimation of  $c_v$  and  $C_v$ .

The density of the metal at 18° C. was found at 21,6 ; calculated : 22,7 ; the meltingpoint is situated at about 2500° C.

Evidently, the value of 3  $R$  calories for  $C_p$  already appears to be surpassed at 100° C.

§ 3. II. The *rhodium* originally used had the form of a coarse powder, which was enclosed within an air-containing crucible. It soon appeared, however, that above 600° C. the weight of the crucible slowly increased, evidently by an absorption of oxygen from the air by the heated metal. For this reason, the experiments were repeated with the metal brought into the shape of globules of the size of a pea. As the  $Q-t$ -curve thus obtained showed, however, still a slightly upwards shape at higher temperatures, suspicion arose that even under these circumstances an oxidation of the metal took place. Indeed, after opening the crucible, it appeared that the metallic spheres at their surfaces had obtained a bluish hue, evidently caused by the formation of a sub- or other oxide. The necessity presented itself, therefore, also in this case to enclose the fresh metal within a completely evacuated platinum vessel ; and this arrangement really allowed us to get the very accurate and reproducible results, a review of which is given in Table II. The values thus obtained are greater than in the case first mentioned, — as may be seen from the following numbers :

Temperature $t$ in °C.:	Amounts of Heat given off between $t^\circ$ and $0^\circ$ C.		Differences in $0/0$ :
	by 1 Gr. of Rhodium heated in air:	by 1 Gr. of Rhodium heated in vacuo:	
	( $Q_0$ in calories)	( $Q_0$ in calories)	
320.8	19.540	19.712	0.87
632.2	39.632	41.018	3.37
814.4	52.902	54.584	3.08
983.5	65.703	67.784	3.07
1201.5	82.962	85.349	2.79
1392.4	99.387	101.374	1.97

From this it becomes clear that, although the metal already takes up

TABLE II. Specific Heats under constant pressure of Rhodium between 0° and 1603° C.

Temperature $t$ in °C.:	Final temperature $t'$ of Calorimeter:	Increase of temperature $\Delta t$ of Calorimeter:	Weight of Rhodium:	Weight of Platinum:	Mean specific heat $c_p$ of Rh between $t$ and $t'$ :	Total amount of Heat given off between $t'$ and 0° by 1 Gr. of Rh (calories):	Total amount of Heat $Q$ delivered between $t$ and $t'$ by 1 Gr. (calories):	Total amount of Heat $Q_0$ given off between $t$ and 0° by 1 Gr. of Rh (calories):
419.50	20.79	0.70920	25.4838	25.500	0.062703	1.2085	25.0006	26.2085
421.82	20.92	0.71321	25.4838	25.500	0.062723	1.215	25.146	26.361
520.90	20.90	0.90328	25.4838	25.500	0.063876	1.226	31.939	33.165
521.36	21.05	0.90374	25.4838	25.500	0.063919	1.234	31.979	33.213
629.77	21.28	1.1164	25.4838	25.500	0.065113	1.236	39.621	40.857
630	21.34	1.1186	25.4838	25.500	0.065283	1.240	39.735	40.975
799.69	21.51	1.4636	25.4838	25.500	0.067099	1.250	52.214	53.464
800.26	21.72	1.4643	25.4838	25.500	0.067103	1.262	52.242	53.504
1000.2	22.20	1.8915	25.4838	25.500	0.069407	1.290	67.875	69.165
1200.4	22.76	2.3398	25.4838	25.500	0.071277	1.322	83.938	85.260
1200.95	22.92	2.3408	25.4838	25.500	0.071277	1.331	83.968	85.299
1391.7	23.30	2.7664	25.4838	25.500	0.073110	1.350	99.990	101.340
1540.65	23.68	3.1006	25.4838	25.500	0.074521	1.380	113.045	114.425
1603.5	23.27	3.2621	25.4838	25.500	0.074735	1.350	118.095	119.445

oxygen at temperatures as low as 321° C., the oxidation only with an appreciable speed sets in at 600° C. or higher. The decrease of the percentual differences at the higher temperatures is explained by the fact, that the oxidation begins at the surface of the metallic spheres and that this surface then is gradually coated with a layer of the oxides formed, which layer prohibits a further oxidation of the metal.

The results finally obtained by using the evacuated crucible, were repeatedly controlled; indeed, they appeared to be reproducible within less than 0,1 % of the total value.

The mean specific heat of *rhodium* between 73° C. and 1,°7 C. was, by means of the supplementary calorimeter previously described, determined at 0,0598; the true specific heat  $c_p$  at 0° C. was calculated at 0,0581.

Now, if from these data one tries to represent the heat  $Q_0$  delivered by an empirical equation of the form:  $Q_0 = A \cdot t + B \cdot t^2 + C \cdot t^3 + D \cdot t^4$ , — it soon appears, that this is possible only between 0° and about 1300° C.:

$$Q'_0 = 0,05893 \cdot t + 0,053299 \cdot 10^{-4} \cdot t^2 + 0,09248 \cdot 10^{-7} \cdot t^3 - 0,044104 \cdot 10^{-10} \cdot t^4 \quad (1)$$

If  $t = 0^\circ \text{C.}$ ,  $c_p$  gets the value: 0,05893, which is in perfect agreement with the number actually observed; while at all other temperatures  $c_p$ , therefore, can be found from the formula:

$$c_p = 0,05893 + 0,01066 \cdot 10^{-3} \cdot t + 0,027744 \cdot 10^{-6} \cdot t^2 - 0,017642 \cdot 10^{-9} \cdot t^3 \quad (1^A)$$

The values of  $Q_0$  at 1391,7°, at 1540,6° and at 1603,5° C., however, as calculated from this equation, all three appear to be too low. As easily may be seen, the equation for  $c_p$  has a *maximum* at 1204° C.

If, however, *all* values for  $Q_0$  should be represented by one and the same formula, then only an equation with at least *five* constants suffices:

$$Q'_0 = 0,054008 \cdot t + 0,0292304 \cdot 10^{-3} \cdot t^2 - 0,028991 \cdot 10^{-6} \cdot t^3 + 0,019564 \cdot 10^{-9} \cdot t^4 - 0,0488144 \cdot 10^{-13} \cdot t^5 \quad (2)$$

The corresponding formula for  $c_p$  is:

$$c_p = 0,054008 + 0,0584608 \cdot 10^{-3} \cdot t - 0,086973 \cdot 10^{-6} \cdot t^2 + 0,078256 \cdot 10^{-9} \cdot t^3 - 0,0244072 \cdot 10^{-12} \cdot t^4 \quad (2^A)$$

it also has a *maximum*, but this is now situated at 1470° C.

This last formula, however, appears unsuitable for temperatures inferior to 420° C.; thus, for instance, the number 0,05401 at 0° C. is much too low, in comparison with the actually found value, and so are all values below ca. 400° C.

The agreement between  $Q'_0$  and  $Q_0$ , as it is calculated from the formulae 1) or 2) respectively, may be seen by comparison of the following numbers:

Temperature $t$ :	$Q_0$ (observed):	$Q'_0$ (calculated from 1):	$Q'_0$ (calculated from 2):
419.50	26.208	26.209	26.203
421.82	26.361	26.361	26.361
520.90	33.165	33.158	—
521.36	33.213	—	33.252
629.77	40.857	40.842	40.959
630	40.975	40.975	40.975
799.69	53.464	53.461	53.461
800.26	53.504	53.504	53.504
1000.2	69.165	69.114	68.946
1200.4	85.260	85.260	85.260
1200.95	85.299	85.286	85.307
1391.7	101.340	100.722	101.540
1540.65	114.425	112.413	114.425
1603.5	119.445	117.172	119.826

In both cases the remarkable fact *remains*, however, that the  $c_p$ — $t$ -curve shows a *rather steep maximum* between 1200° and 1400° C., and probably nearer to the first temperature than to the latter.

§ 4. The question may arise, whether *rhodium* also will show such an abnormal dependancy on temperature for others of its physical properties? In literature the singular position of the metal with respect to its *magnetic susceptibility* was first pointed out by HONDA <sup>1)</sup>. This author found, that in contrast with the behaviour of *palladium* and *platinum*, the specific magnetic susceptibility  $\chi$  of the likewise paramagnetic *rhodium*, *increases* almost linearly with the temperature between 24° and 1143° C.; at 24° C. the value of  $\chi$  is  $+1.14 \cdot 10^{-6}$ , at 1143° C.:  $\chi = +1.86 \cdot 10^{-6}$ . A discontinuity in this respect was, however, not found.

Also for the *temperature-coefficient of the electrical resistance* we were unable to state a sudden break in the curve representing these values as a function of temperature. We are indebted to Professor HOLST and Dr. P. CLAUSING of the *Scientific Laboratory of the PHILIPS' Incandescent Lamp-Works* at *Eindhoven* for furnishing us with an incandescent lamp, prepared of a *rhodium*-wire and carefully exhausted. The wire could be heated by means of an electrical current of exactly known intensity; its

<sup>1)</sup> K. HONDA, Science Rep. Tohoku Univ. I, 1. (1911), 30, 32, 33, 34; Ann. der Phys., (4), 32, (1910), 1059; conf. also: M. OWEN, Ann. d. phys., (4), 37, (1912) 698.



temperature was checked by means of a calibrated HOLBORN—KURLBAUM-pyrometer. Two joints of *rhodium*-wire were applied sideways, and between these two points of the wire the voltage could exactly be measured.

The resistance of the wire at each temperature at increasing temperatures appeared always slightly lower than at decreasing temperatures; but both curves were, in general, quite parallel, the small deviations only being caused by little differences in the temperatures of the conducting parts of the lamp in both series of experiments and by the different temperature-readings.

For a wire of 0.3 mm diameter and about 17 cm length, the following (approximative) values of the electrical resistance were observed:

*A. At increasing temperatures:*

Temperature in °C.:										
660°	690°	780°	790°	850°	865°	910°	970°	1040°	1140°	1230°
Resistance in Ohms:										
0°394	0.414	0.475	0.483	0.522	0.533	0.566	0.618	0.693	0.782	0.857

*B. At decreasing temperatures:*

Temperature in °C.:									
1210°	1150°	1100°	1070°	980°	940°	890°	820°	740°	660°
Resistance in Ohms:									
0.854	0.810	0.772	0.734	0.647	0.607	0.563	0.513	0.641	0.410

If these values of the resistance are plotted against the temperature, a curve of the form represented in Fig. 1 is obtained. The form of this curve, showing a turning-point *W* between 1000° and 1100° C., is in perfect qualitative agreement with the results obtained in 1895 by HOLBORN and WIEN by means of another method. Although their results cannot directly be compared with ours, because the dimensions of their wire are not known. — an impression of the form of their curve (at a scale of 1 : 10) may be got from the broken line in Fig. 1. They also find a turning-point *w* between 1000° and 1100° C., the form of the curve below *w* being convex,

1) L. HOLBORN and W. WIEN. *Ann. der Physik*, N. F., **56**, (1895), 385.

above  $W$  concave towards the temperature-axis. With all other metals, as for instance, *palladium* or *platinum*, the curve is always concave towards the temperature axis <sup>1)</sup>, — even if the metal is not quite pure. Most probably our *rhodium* is purer than theirs was, — which partially may account for the steeper slope of the curve as found by us.

Although certainly there is an abnormality present here, — which is, as we will see, connected with a gradual change in the internal structure of the wire, — the dependance of its properties on temperature, also in this respect, remains quite *continuous*, without, therefore, there being any sudden break in the curve.

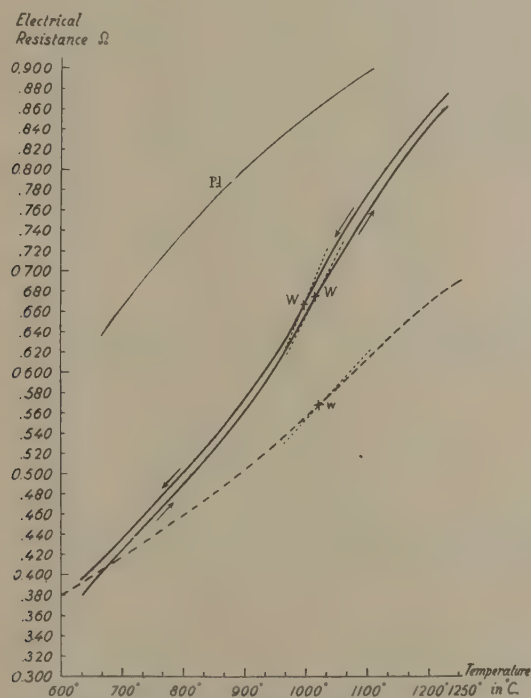


Fig. 1. Electrical Resistance of Rhodium-Wire as a Function of the Temperature.

In this connection it is worth to emphasise that we also made the same experiments with a wire of pure *palladium*. It appeared, however, that in this case the curve representing the electrical resistance as a function of the temperature, has the *normal* shape, it being over its whole length concave towards the temperature-axis. The abnormal behaviour of the  $c_p$ — $t$ -curve of this metal in the neighbourhood of the melting-point has, therefore, another significance than that of *rhodium*.

<sup>1)</sup> loco cit., 384.

§ 5. In the hope perhaps to find another indication of some allotropic transformation occurring in the metal, we now proceeded to determine the *thermoelectric force* of purest *rhodium* with respect to pure *platinum* at all temperatures between  $0^{\circ}$  and  $1604^{\circ}$  C.

The wire, made of purest *rhodium*, also had a diameter of 0.3 mm. It was soldered in the electric arc to a similar wire of purest *platinum* and the electromotive force of the thermo-couple thus formed was determined in the usual way, the hot junction being placed into a small platinum vessel, the cold one constantly being kept at  $0^{\circ}$  C. in the ice-box. No break in the curve representing the electromotive force  $E$  in function of  $t$  could, however, be detected. The values of  $E$  obtained on heating were practically identical with those obtained by cooling. At  $0^{\circ}$  C. a small correction must be applied of + 11 M.V. as a result of the electromotive force caused by the attachment of the *rhodium*-wire to the metallic connection in the ice-box. If this correction is taken into account, the electromotive force  $E$  of the thermocouple in function of the temperature  $t$  can, between  $400^{\circ}$  and  $1600^{\circ}$  C., very accurately be represented by the empirical equation :

$$E = 6,06104 \cdot t + 0,0112014 \cdot t^2 - 0,06663 \cdot 10^{-4} \cdot t^3 + \\ + 0,04664 \cdot 10^{-7} \cdot t^4 - 0,013036 \cdot 10^{-10} \cdot t^5.$$

Reversely, the temperature  $t$ , as measured by this thermo-couple, can, between the limits indicated, be calculated from its thermoelectric force  $E$ , by means of the equation :

$$t = 0,0135635 \cdot E - 0,0110538 \cdot 10^{-3} \cdot E^2 + 0,07949 \cdot 10^{-8} \cdot E^3 - \\ - 0,029425 \cdot 10^{-12} \cdot E^4 + 0,04129 \cdot 10^{-17} \cdot E^5.$$

In both equations  $E$  is expressed in microvolts,  $t$  in degrees centigrade : the coefficients were calculated from the following data :

$t$ :	$E$ (corrected):
$350^{\circ}$ C.	3271 M.V.
$600^{\circ}$	6733
$900^{\circ}$	11961
$1200^{\circ}$	18317
$1600^{\circ}$	27978

The results are practically identical with those obtained by DAY and SOSMAN<sup>1)</sup>.

As an example of the agreement between the observed and calculated values, the following numbers can be considered :

<sup>1)</sup> See: A. L. DAY and R. B. SOSMAN, CARNEGIE-Publication, 157, Washington, (1911), p. 121, 122.

$t$ in $^{\circ}\text{C}.$ :	$E$ (observed):	$E$ (calculated):	$E$ (in M.V.):	$t$ (in $^{\circ}\text{C}.$ ): (calculated)
0°	0	0	0	0'
100	—	712	1000	125.35
200	—	1614	2000	232.96
300	—	2681	3000	326.60
400	3867	3896	4000	409.44
500	5221	5249	5000	484.1
600	6733	6733	6000	554.7
700	8341	8347	10000	792.9
800	10097	10090	15000	1034.3
900	11961	11961	16000	1101.2
1000	13951	13960	18000	1187.5
1100	16101	16082	19000	1226.8
1200	18317	18317	20000	1264.1
1300	20617	20652	25000	1442.1
1400	22991	23063	(29000)	(1684)
1500	25443	25506	(30000)	(1790)
1600	27978	27978	—	—

The small deviation above  $1250^{\circ}\text{C}.$  of the two curves in Fig. 2 is of no significance, as it only is caused by the fact, that the one equation is not exactly the inverse one of the other. Perhaps only an equation with more than five constants would bring about a closer agreement.

§ 6. All these experiments, especially those concerning the specific heats and the specific electrical resistance, prove that, — although *rhodium* shows some unexplained particularities, — the physical properties evidently vary with temperature in a quite continuous way: in no case a sudden break in the curves ever was observed. This fact, however, does not exclude the possible existence of allotropic modifications; it were, for instance, very well possible that a kind of dynamical equilibrium between such forms at each temperature would exist. In that case the relative masses of both modifications would continuously vary with the temperature; and the observed physical behaviour would always be a *mean* value, depending on the ratio of both forms in the mixture studied.

We, therefore, have tried to prove the existence of such allotropic modifications in the metal by a careful and very elaborated *X-ray-analysis*

of its structure. As well *rhodium* obtained by electrolytical deposition from solutions or by reduction with hydrazine-sulphate, as *rhodium* in the form

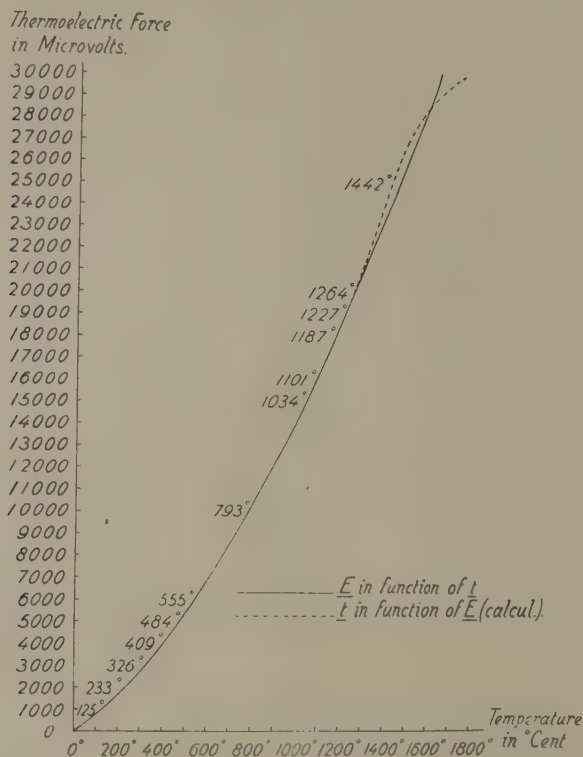


Fig. 2. Thermoelectric Force of Rhodium against Platinum between 0° and 1600° C.

of wire were studied at different temperatures ranging from 20° to 1500° C. As may be seen from a former paper<sup>1)</sup>, we were able in this way to prove, that, while *rhodium* at higher temperatures crystallises in a face-centred cubic lattice with  $a_0 = 3,79 \text{ \AA}$ ., the electrolytically deposited product is a mixture of *two* modifications in variable proportions. The one is the same  $\beta$ -modification mentioned above; the other is a different  $\alpha$ -modification, which exists besides the other at all temperatures at least below 1000° C., — its quantity gradually diminishing with an increase of temperature. Above 1400° C. no trace of the  $\alpha$ -form could any more be observed. Although by the lack of suitable crystals, it was hitherto impossible to get full information of its real crystal-structure, — it seems certain that the  $\alpha$ -modification is also a cubic one, with a simple cubic lattice and a parameter  $a_0 = 9,211 \text{ \AA}$ ., its elementary cell having a much

<sup>1)</sup> F. M. JAEGER and J. E. ZANSTRA, These Proceedings, **34**, p. 15.



greater volume<sup>1)</sup> and containing 48 atoms of *rhodium*. Its density, therefore, is smaller than that of the  $\beta$ -modification; no appreciable heat-effect seems to accompany its transformation into the other form.

As to the specific heat, — the question may arise, whether the maximum in its temperature-curve can be accounted for, without there evidently being any appreciable additional heat-effect superimposed upon the heat emitted by the metal on cooling? The answer is, that, according to experience, it is absolutely necessary to acknowledge such a possibility: it is erroneous to suppose, that a maximum in the  $c_p$ — $t$ -curve necessarily should have much to do with such an "additional" amount of heat, the latter being given off as "heat of transformation" of allotropic modifications changing into each other in a reversible way. As a corroboration of this assertion, we will remind here of the cases of  $\alpha$ - and  $\beta$ -iron and of  $\alpha$ - and  $\beta$ -nickel: in both cases there is a sudden and very appreciable change of the specific heat at the transition-temperatures<sup>2)</sup>; in the case of *nickel*, for instance, the curves for  $c_p$  and  $c_v$  in function of the temperature even show a maximum between 100° and 400° C., not coinciding with the transition-temperature itself<sup>3)</sup>. But the heat of transformation for  $\alpha \rightarrow \beta$ -*nickel* is not greater than 0.013 calorie per gramme<sup>4)</sup>, that of  $\alpha$ - and  $\beta$ -iron not greater than 6.56 calorie per gramme<sup>5)</sup> — both values, which are *quite inconsiderable* as a contribution to the heat-emission of the metals in the calorimeter. Perhaps the specific heat is one of those physical properties, which are most sensitive for even very slight changes in the internal arrangement of the composing atoms, — be it into another lattice or merely into a more or less pronounced aggregation of structural individuals. In the two cases mentioned above, there is not even an appreciable change of specific volume accompanying the said transformations; the considerable changes of the specific heats here, evidently are wholly depending upon the even apparently insignificant variations in the internal structure of the solid phases considered. It is this factor, which no theory of specific heats at higher temperatures hitherto could account for; and this is the cause, why each theory has failed to explain the facts observed, at least in a satisfactory way.

## § 7. The approximate values of the specific heats of *rhodium* at

<sup>1)</sup> P. WEISS, A. PICCARD and A. CARRARD, Arch. des Sc. nat. et phys. Genève, **12**, (1916), 378; **43**, 22, 113, 199; (4), **122**, (1917), 378.

<sup>2)</sup> P. SCHÜBEL, Zeits. f. anorg. Chemie **87**, (1914), 91.

<sup>3)</sup> M. WERNER, ibidem, **83**, (1913), 313, 321.

<sup>4)</sup> Several lines of the spectrogram of the  $\beta$ -modification coincide almost completely with certain diffraction-lines of the  $\alpha$ -modification. This fact explains the broadening out of the lines of the latter form, as is regularly observed in its spectrograms.

<sup>5)</sup> A. MEUTHEN, Dissert. Aachen, (1915); F. DURRER, Dissert. Aachen, (1915); H. BREDEMEIER, Zeits. f. anorg. Chem. **151**, (1926), 112.

constant volume  $c_v$  can, as far as  $1300^\circ \text{C.}$ , be calculated from the general thermodynamical expression for  $(c_p - c_v)$ .

The thermal dilatation was determined by FIZEAU <sup>1)</sup> and VALENTINER and WALLOT <sup>2)</sup>; the first for the linear coefficient  $\alpha$  found the value: 0,00000858; the German investigators determined  $\alpha$  at  $50^\circ \text{C.}$  at: 0,00000876. Although these data are insufficient, the cubic expansion-coefficient  $3\alpha$  can, — in analogy with the behaviour of *palladium*, — roughly be estimated at about:  $0,00002638 + 0,000000012 \cdot t$ . The compressibility, at the other hand, was measured by BRIDGMAN <sup>3)</sup>: at  $30^\circ \text{C.}$ ; he found for  $\kappa$  (in K.G. pro  $\text{cm}^2$ ):  $\kappa \cdot 10^6 = 0,372 - 2,67 \cdot 10^{-6} \cdot p$  and at  $75^\circ \text{C.}$ :  $\kappa \cdot 10^6 = 0,381 - 2,67 \cdot p$ .

The approximate values of  $c_v$  and the atomic heat  $c_v$  thus calculated, are given in the following table:

$t$ in $^\circ \text{C.}$ :	$c_p$ :	$c_v$ (approx.):	$C_p$ :	$C_v$ (approx.):
$0^\circ$	0.05893	0.05793	6.064	5.961
100	0.06026	0.06013	6.201	6.063
200	0.06203	0.06186	6.383	6.200
300	0.06415	0.06393	6.601	6.362
400	0.06650	0.06623	6.843	6.546
500	0.06899	0.06866	7.099	6.742
600	0.07150	0.07111	7.357	6.938
700	0.07393	0.07348	7.607	7.125
800	0.07618	0.07566	7.839	7.293
900	0.07814	0.07755	8.041	7.429
1000	0.07969	0.07903	8.200	7.521
1100	0.08074	0.08001	8.308	7.559
1200	0.08119	0.08038	8.354	7.530
1300	0.08092	0.08008	8.327	7.422

If calculated from the second formula, the values of  $c_p$  and  $C_p$  at  $400^\circ \text{C.}$  will appear about 2 %, at  $1300^\circ \text{C.}$  about 5 % greater than those given in this table, the maximum being shifted to  $1470^\circ \text{C.}$  in stead of  $1204^\circ \text{C.}$

In every case, — even for  $C_v$ , — the value of  $3R$  appears already to be surpassed at a temperature of about  $100^\circ \text{C.}$

<sup>1)</sup> H. FIZEAU, Compt. rend. Paris, **68**, (1869), 1175.

<sup>2)</sup> S. VALENTINER and J. WALLOT, Ann. d. Phys. **46**, (1915), 837.

<sup>3)</sup> P. W. BRIDGMAN, Proceed. Nat. Acad. America, **59**, (1923), 110, 111.

Finally the curves for  $C_p$  and for  $C_v$  are graphically represented in Fig. 3. as well for rhodium, as for osmium; for the purpose of comparison, those for platinum and palladium are added on the same scale.

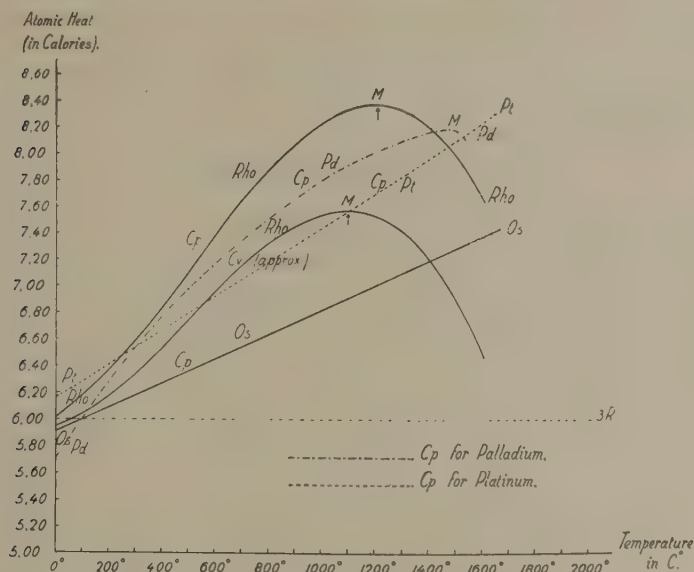


Fig. 3. Atomic Heats  $C_p$  and  $C_v$  of Rhodium and  $C_p$  of Osmium.

Groningen, Laboratory for Inorganic and Physical  
Chemistry of the University.

**Mathematics.** — *Ueber freie Umschliessungen im Raume.* Von L. E. J. BROUWER.

(Communicated at the meeting of January 31, 1931).

In meiner Arbeit „Ueber Jordansche Mannigfaltigkeiten“ (Math. Ann. 71 (1911), S. 320—327) habe ich bewiesen, dass im  $n$ -dimensionalen Cartesischen Raume jeder Punkt einer Jordanschen Mannigfaltigkeit sowohl für das innere wie für das äussere Gebiet erreichbar ist. Im Anschluss an diesen Satz habe ich die evidente, aber im dortigen Zusammenhange trotzdem zu erwähnende Tatsache hervorgehoben, dass eine freie Umschliessung im  $n$ -dimensionalen Cartesischen Raume (d.h. eine geschränkte abgeschlossene Punktmenge, welche im  $R_n$  zwei Gebiete bestimmt, und von der jeder Punkt für jedes dieser Gebiete erreichbar ist) nicht notwendig eine Jordansche Mannigfaltigkeit, nicht einmal notwendig zusammenhängend im kleinen ist. Anschaulich formuliert, erhält man nämlich im dreidimensionalen Euklidischen Raume sofort eine nicht-Jordansche freie Umschliessung, wenn man von zwei sich gegenüberliegenden parallelen Kanten eines Kubus die Mittelstrecken zusammennäht, und eine nicht im kleinen zusammenhängende freie Umschliessung, wenn man am horizontalen oberen Grenzquadrat des Einheitskubus längs einer Diagonale eine gegen eine vertikale Kante konvergierende Fundamentalreihe von vertikalen hinreichend engen Einstülpungen der Tiefe  $\frac{1}{2}$  vornimmt.

Im a.a.O. S. 321 gegebenen formelhaften Beispiel, das diese Tatsache analytisch beschreiben soll, hat sich aber ein Versehen eingeschlichen: es muss das in den Formeln auftretende  $\cos \varphi$ , um eine nicht-Jordansche freie Umschliessung zu erhalten, durch  $\cos 2\varphi$ , und um eine nicht im kleinen zusammenhängende freie Umschliessung zu erhalten, durch  $\cos 2\varphi \cdot \operatorname{sgn} \sin \left( \varphi + \frac{1}{4} \pi \right)$  ersetzt werden.

Den Anlass zur Publikation dieser auf der Hand liegenden Richtigstellung bildet eine neuerdings in den Comptes-Rendus vom 5.1.1931 (Bd. 192) veröffentlichte Note von Herrn REY PASTOR, die mein oben zitiertes Beispiel zum Gegenstand hat, und in welcher der Versuch, das Beispiel durch ein besseres zu ersetzen, nicht gelungen ist; zur daselbst definierten angeblichen nicht-Jordanschen freien Umschliessung gehören nämlich die Punkte  $\varrho = 0$ ,  $1 < z \leq \sqrt{2}$ , welche von unten nicht erreichbar sind, so dass keine freie Umschliessung vorliegt. Um auf dem Wege, der

Herrn REY PASTOR vorgeschwebt hat, das Beispiel in Ordnung zu bringen, muss in den zitierten Formeln meiner Arbeit das  $\cos \varphi$  durch  $\cos \varphi \cdot s_2(\varphi)$  bzw. durch  $\cos \varphi \cdot s_4(\varphi)$  ersetzt werden; hierin stellt  $s_2(\varphi)$  bzw.  $s_4(\varphi)$  die Winkelfunktion vor, die für  $\varphi \neq n\pi$  bzw. für  $\varphi \neq \frac{n}{2}\pi$  den absoluten

Wert 1 besitzt, für  $\varphi = 1$  positiv ist, und für  $\varphi = n\pi$  bzw. für  $\varphi = \frac{n}{2}\pi$  einerseits das Zeichen wechselt, andererseits daselbst alle Werte des geschlossenen Intervalls  $(-1, +1)$  annimmt.

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Mathematics. — Die Komitanten des Konnexes  $\Sigma A_{ik,\lambda} \Pi_{ik} x_i$ .

Von R. WEITZENBÖCK.

(Communicated at the meeting of January 31, 1931).

Ich stelle im Folgenden ein kleinstes volles System von projektiven Komitanten der quaternär-binären Form  $F = \Sigma A_{ik,\lambda} \Pi_{ik} x_i = \frac{1}{2} (A' \Pi)^2 a_x$  auf, wo also die  $\Pi_{ik}$  ( $i, k = 1, 2, 3, 4$ ) PLÜCKERSche Linienkoordinaten im dreidimensionalen Raume und die  $x_\lambda$  ( $\lambda = 1, 2$ ) binäre Koordinaten bedeuten. Das volle System besteht aus 13 Komitanten, darunter eine einzige Invariante vom Grade vier in den Koeffizienten von  $F$ . Am Schlusse bespreche ich die geometrische Bedeutung der einfachsten dieser Komitanten.

### § 1.

Wir bezeichnen Reihen aus dem quaternären Gebiete mit grossen, aus dem binären Gebiete mit kleinen Buchstaben. Sei

$$F = \frac{1}{2} (A' \Pi)^2 a_x = \frac{1}{2} (A \Pi')^2 a_x = \Sigma A_{ik,\lambda} \Pi_{ik} x_\lambda \quad . \quad . \quad . \quad (1)$$

die gegebene Grundform mit den  $2 \cdot 6 = 12$  Koeffizienten  $A_{ik,\lambda}$ .

An Symbol- und Grössenreihen stehen dann zur Verfügung:

$$A, B, \dots, \Pi, X; A', B', \dots, \Pi', U'; a, b, \dots, x \quad . \quad . \quad . \quad (2)$$

woraus sich, da wir wegen der Komplexsymbole von quaternären Klammerfaktoren absehen können, die folgenden Faktortypen bilden lassen:

$$(AB'), (A \Pi'), (A U'); (A' X), (A' \Pi), (X \Pi'), (U' \Pi), (U' X) \left\{ \begin{array}{l} (ab), \quad a_x = a_1 x_1 + a_2 x_2 \end{array} \right. \quad . \quad (3)$$

Hier ist  $(U' X)$  bereits eine Komitante und  $(\Pi' P)$  ( $P$  äquivalent mit  $\Pi$ ) ist als Reducent nicht mehr angeschrieben. Beim Aufbauen der Produkte aus diesen Faktoren achten wir zuerst auf die quaternären Reihen und bilden mit den Komplexsymbolen sogenannte "Ketten"

$$[XA' BC' D \dots] = (XA') (A' B) (BC') (C' D) \dots$$

Nachdem allgemein

$$(XA') (A' \Pi) (\Pi U') = - (X \Pi') (\Pi' A) (A U') - \frac{1}{2} (A' \Pi)^2 \cdot (X U') \quad . \quad (4)$$

gilt, kann man in einer Kette zwei benachbarte Buchstaben miteinander vertauschen, wenn man gleichzeitig das Vorzeichen umkehrt. Hieraus folgt, dass zu jedem Faktor  $(A' B)$  ein binärer Klammerfaktor  $(ab)$  gehört. Nach (4) ist nämlich:

$$K = (XA') (A' B) (B U') a_x b_y = - (X B') (B' A) (A U') a_x b_y - \frac{1}{2} (A' B)^2 (U' X) a_x b_y,$$

also, wenn rechts  $A$  mit  $B$  vertauscht wird:

$$K = \frac{1}{2} (XA') (A' B) (B U') (ab) (xy) - \frac{1}{4} (A' B)^2 (U' X) a_x b_y \quad . \quad (5)$$

Hieraus schliessen wir weiter, dass die Anordnung  $A B' C$  in einer Kette zur Reduktion führt. Sei nämlich

$$K = (XA') (A'B) (BC') (C'Y) (ab) c_x = [XA'B C'Y] (ab) c_x$$

und stellen wir in  $[XA'BC'Y]$  mit Hilfe von (4) alle Permutationen der drei Buchstaben  $A, B$  und  $C$  her und addieren, so ergibt sich wegen  $(bc)a_x + (ca)b_x + (ab)c_x \equiv 0$ :

$$K \equiv \frac{1}{6} (AB')^2 (C'X) (C'Y) (bc) a_x \dots \dots \dots (6)$$

Aus (3) ergeben sich dann aus den quaternären Faktoren die folgenden "Radicale":

$$\left. \begin{aligned} \pi_1 &= (XA') (A'II) a_\xi & \pi'_1 &= (U'A) (AII') a_\xi \\ \pi_2 &= (XA') (A'B) (BII') (ab) & \pi'_2 &= (U'A) (AB') (B'II) (ab) \\ G &= (XA') (A'B) (BU') (ab) \\ f_2 &= (AB')^2 a_\xi b_\eta & f_\pi &= (AII')^2 a_\xi \\ f_{\pi\rho} &= (IIA') (A'B) (BP') (ab) \\ f_1 &= (II'X) & f'_1 &= (III') \end{aligned} \right\} \quad (7)$$

Hier ist  $G$  bereits eine Komitante. Alle übrigen sind aus diesen Radicalen aufzubauen, wobei quaternär mit den Reihen  $II, II'$ , und binär mit den Reihen  $a, b, \dots$  zu koppeln ist.

Würde bei  $\pi_2$  ein  $(II'C)$  anschliessen, so ergäbe sich die Kette  $[XA'BII'C \dots]$ , die nach (4) und (6) reduzierbar ist. Somit muss  $(II'X)$  anschliessen und dual bei  $\pi'_2$  der Faktor  $(III')$ . Dies gibt die zwei Komitanten

$$F_X = (XA') (A'B) (BII') (II'X) (ab), F_U = (U'A) (AB') (B'II) (III') (ab) \quad (8)$$

und wir können von  $\pi_2$  und  $\pi'_2$  in (7) absehen. Aus demselben Grunde sind  $f_{\pi\rho}$  und die Koppelungen  $\pi_1 - \pi_1, \pi'_1 - \pi'_1$  Reducenten.

Somit finden wir aus (7) nur die folgenden Radicale, die weiterhin nur noch binär zu kombinieren sind:

$$\left. \begin{aligned} p_\xi &= (XA') (A'II) (III') a_\xi \\ q_\xi &= (U'A) (AII') (II'X) a_\xi \\ r_\xi &= f_\pi = (AII')^2 a_\xi \\ f_2 &= (AB')^2 a_\xi b_\eta = a_\xi a_\eta \end{aligned} \right\} \dots \dots \dots (9)$$

Zwischen den drei ersten haben wir nach (4) die Beziehung

$$p_\xi + q_\xi = -\frac{1}{2} (U'X) \cdot r_\xi,$$

sodass also z.B.  $q_\xi$  weggelassen werden kann. Es bleiben dann in (9) zwei binäre Linearformen  $p_\xi$  und  $r_\xi$  und die binäre quadratische Form  $a_\xi^2$ , woraus sich die folgenden Komitanten bilden lassen:

$$p_x, r_x, (pr), (ap)_{a_x}, (ar)_{a_x}, (ap)^2, (ar)^2, (ap)(ar) \text{ und } (a\beta)^2 \dots \dots (10)$$

Hier ist

$$J = (\alpha\beta)^2 = (AB')^2 (CD')^2 (ac) (bd) \quad . \quad . \quad . \quad . \quad (11)$$

die einzige Invariante der Grundform (1).

Man beweist dann leicht durch Spezialisierung der Variablenreihen, dass alle bisher genannten Komitanten nicht reduzibel sind mit Ausnahme von  $(ap)^2$ , das ganz und rational durch die übrigen Komitanten ausdrückbar ist. Formen wir nämlich das Produkt

$F_U \cdot F_X = (XA') (A'B) (BII') (II'X) \cdot (U'C) (CD') (D'P) (PU') (ab) (cd)$   
der beiden Komitanten (8) identisch um, indem wir das Produkt

$$(BII') (II'X) \cdot (CU') (CD') = \frac{1}{4} (\Pi^2 BX) (C'^2 U'D')$$

nach der Identität

$$(\Pi^2 BX) (C'^2 U'D') = \begin{vmatrix} (UC') (\Pi C') (\Pi U') (\Pi D') \\ (\Pi C') (\Pi C') (\Pi U') (\Pi D') \\ (BC') (BC') (BU') (BD') \\ (XC') (XC') (XU') (XD') \end{vmatrix}$$

ausrechnen, so ergibt sich:

$$(ap)^2 = (pr) \cdot G + F_X \cdot F_U - \frac{1}{2} (U'X) \cdot (ap) (ar) \quad . \quad . \quad . \quad (12)$$

Ein kleinstes volles System besteht somit aus 13 Komitanten, die wir in der folgenden Tabelle zusammenstellen:

Reihen	Symbolischer Ausdruck	Grad in den				
		$A_{ik,\lambda}$	$X_i$	$\Pi_{ik}$	$U'_i$	$x'_\lambda$
Invariante	$J = (\alpha\beta)^2 = (AB')^2 (CD')^2 (ac) (bd)$	4				
$X, U'$	$G = (XA') (A'B) (BU') (ab)$	2	1		1	
	$(U'X)$		1		1	
$\Pi, x$	$F = (A\Pi')^2 a_x$	1		1		1
	$(ar)^2 = (ac) (bd) (C'D')^2 (A\Pi')^2 (BP')^2$	4		2		
	$(ar)a_x = (ac) b_x (A'B)^2 (C\Pi')^2$	3		1		1
$x$	$S = a_x^2 = (AB')^2 a_x b_x$	2				2
$X, \Pi$	$F_X = (XA') (A'B) (BII') (II'X) (ab)$	2	2	1		
$U', \Pi$	$F_U = (U'A) (AB') (B'II) (\Pi U') (ab)$	2		1	2	
$X, \Pi, U'$	$p_x = (XA') (A'II) (\Pi U') a_x$	1	1	1	1	1
	$(pr) = (XA') (A'II) (\Pi U') (ab) (BP')^2$	2	1	2	1	
	$(ap)a_x = (XA') (A'II) (\Pi U') (ab)c_x (B'C)^2$	3	1	1	1	1
	$(ap)(ar) = (XA') (A'II) (\Pi U') (ab) (cd) (B'D')^2 (C'P)^2$	4	1	2	1	

## § 2.

Wir besprechen noch kurz die wichtigsten geometrischen Anwendungen der Komitanten des vollen Systems. Wir deuten die Veränderlichen  $\Pi_{ik}$  der Grundform (1) als PLÜCKERSche Linienkoordinaten in einem linearen  $G_4$  ( $\equiv$  projektiver dreidimensionaler Raum) und die  $x_1 : x_2$  als binäre Koordinaten eines Punktes  $x$  auf einer Geraden  $g$ .

Bei gegebenem  $x$  stellt dann  $F=0$  einen linearen Strahlenkomplex  $K_x$  in  $G_4$  dar. Er ist speziell für

$$S = \alpha_x^2 = (AB')^2 a_x b_x = 0,$$

also für zwei Punkte  $s_1$  und  $s_2$  auf  $g$ . Sie fallen zusammen wenn die Discriminante  $(\alpha\beta)^2$  von  $S$ , also die Invariante  $J$  (Vgl. die Tabelle) verschwindet. Die beiden durch  $(A'\Pi)^2 a_{s_i} = 0$  dargestellten Geraden  $L_1$  und  $L_2$  sind dann die Leitlinien der linearen Kongruenz  $C$ , deren Geraden allen Komplexen  $K_x$  gemeinsam sind. Für das Produkt  $L_1 L_2$  findet man leicht die Gleichung  $(ar)^2 = 0$  (Vgl. die Tabelle).

Umgekehrt gibt  $F=0$  bei gegebenem  $\Pi_{ik} = P_{ik}$ , wenn  $(A'P)^2 a_x \equiv 0 \{x\}$  ist, einen Punkt  $s_p = (A'P)^2 a_x = 0$  auf der Geraden  $g$ . Den  $\infty^2$  Geraden  $Q_{ik}$  aber, für die  $(A'Q)^2 a_i = 0$  ( $i=1, 2$ ) ist, entspricht kein Punkt auf  $g$ ; sie erfüllen dieselbe Kongruenz  $C$ , deren Leitlinien durch  $(ar)^2 = 0$  gegeben sind.

Wir haben damit für  $J \neq 0$  die folgende Figur: den beiden Punkten  $s_1$  und  $s_2$  auf  $g$  ordnet  $F=0$  zwei Gerade  $L_1$  und  $L_2$  zu, jedem Punkte  $s_1 + \lambda s_2$  von  $g$  entspricht der lineare Komplex  $L_1 + \lambda L_2$  und umgekehrt. Für alle Geraden die  $L_1$  und  $L_2$  schneiden und nur für diese ist  $F \equiv 0 \{x\}$ . Sucht man zu einem Punkte  $x$  auf  $g$  den Pol bezüglich  $\alpha_x^2 = 0$ , so entspricht diesem der durch  $(ar)\alpha_x = 0$  (Vgl. die Tabelle) dargestellte lineare Komplex.

Ist  $\Pi_{ik}$  eine Gerade, so bestimmt sie mit  $L_1$  und  $L_2$  zusammen eine Fläche zweiter Ordnung und Klasse, deren Gleichung in Punkt- bzw. in Ebenenkoordinaten durch  $F_x = 0$  bzw. durch  $F_u = 0$  gegeben ist.

Von den übrigen Komitanten wollen wir noch kurz die Zwischenform  $G$  geometrisch deuten. Halten wir z.B. den Punkt  $X$  fest, so stellt  $G=0$  einen Punkt  $Y$  dar, den man wie folgt konstruieren kann. Die beiden Leitlinien  $L_1$  und  $L_2$  werden durch  $(A'\Pi)^2 a_{s_i} = 0$  gegeben. Wir legen durch  $X$  die Gerade  $T$ , die  $L_1$  in  $S_1$  und  $L_2$  in  $S_2$  schneidet;  $Y$  ist dann der zu  $X$  harmonisch bzgl.  $S_1$  und  $S_2$  liegende Punkt. Wir haben nämlich

$$(U'S_2) = (XA')(A'B)(BU') a_{s_1} b_{s_2} = \\ = - (XA')(A'B)(BU') a_{s_2} b_{s_1} - \frac{1}{2} (A'B)^2 a_{s_1} b_{s_2} \cdot (U'X) \\ (U'S_1) = (XA')(A'B)(BU') a_{s_2} b_{s_1};$$

also wird:

$$(U'S_1) + (U'S_2) = - \frac{1}{2} (A'B)^2 a_{s_1} b_{s_2} \cdot (U'X)$$

$$(U'S_1) - (U'S_2) = (XA')(A'B)(BU')(ab)(s_1 s_2) = (U'Y) \cdot (s_1 s_2),$$

dh.  $S_1, S_2, X$  und  $Y$  liegen harmonisch und  $G=0$  gibt die geschaarte Involution mit den beiden Doppellinien  $L_1$  und  $L_2$ .

**Anthropology.** — *Contributions to the Anthropology of the Near East.*  
III. *Phoenician and Palmyrene Skulls.* By C. U. ARIËNS KAPPERS.

(Communicated at the meeting of January 31, 1931).

My researches concerning the anthropology of the Semitic races in the Near East were greatly favored by the possibility of studying a number of Phoenician skulls, one from Byblos (Djebail) and fifteen from Sidon (Saïda), two Palmyrene skulls and two Hebrew skulls of Solomon's time, found at Megiddo. Of the latter I shall speak again in my next paper.

I am much indebted to the conservator of the National Museum at Beirut, the Ameer M. CHEHAB, for allowing me to measure and photograph the Phoenician skulls and to the representatives of Mr. P. L. O. GUY, of the Oriental Institute of Chicago, excavating Megiddo, for being allowed to see and measure the ancient skulls of Megiddo.

I also want to express my thanks to Father BERGY of the Université St. Joseph at Beirut for his permission to measure and photograph the ancient Semitic skull he found in a riverbed in the Beka, the valley between the Lebanon and Anti-Lebanon.

In addition I measured the heads of 107 males of more or less nomadic Arab tribes, Beduins of the North-Syrian desert from the surroundings of Palmyra, Aleppo, Selemiye (north west desert), several from Deir-el-zore (north east desert), whom I met near Aleppo, and some Hauran Beduins (Beni-Darra). To the same group belong some Arabs of the Hedjaz and Nedjd and some from Bahrein (in the Persian gulf).

As a closely related group I measured the heads of 117 Egyptian Arabs. Also 139 Palestinian Arabs were measured, but I shall discuss the latter in my next paper.

Most Phoenician skulls hitherto described came from Africa, and from European sites round the Mediterranean. Although their Phoenician (Punic) origin in most cases could be stated with certainty by the fact that they were found in Phoenician colonies and in Phoenician tombs or at least amongst Phoenician remains, they do not belong to the oldest period as the great Phoenician transmarine settlements (chiefly from Tyre) only commenced after the 9<sup>th</sup> century B.C.

DE QUATREFAGES and HAMY<sup>1)</sup> described twelve Punic skulls from Utica near Carthage with an average index for the males of 74.86, for the females of 73.37. It is very likely that the lower female index is incidental,

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<sup>1)</sup> DE QUATREFAGES et HAMY. *Crania ethnica. Les crânes des races humaines*, Paris, 1882, Quoted from BERTHOLON and CHANTRE, the original not being at my disposal.



the female index being usually higher than the male, especially with the Arabic Semites (see below).

So BERTHOLON<sup>1)</sup>, who examined two probably female skulls from Bulla Regia and Carthage found an average index of 77.8 (one of 77.5 and one of 78.07). BERTHOLON and CHANTRE<sup>2)</sup> who examined 68 male and 49 female crania from Carthage found an average male index of 74.98, an average female index of 75.85 thus showing that also here the female index is higher.

It is an interesting fact that of the crania mentioned by BERTHOLON and CHANTRE, belonging to the 6<sup>th</sup> to 3<sup>rd</sup> century B.C., those of the 3<sup>rd</sup> century are far more dolichocephalic than the others, suggesting that especially amongst the latter there are many admixture with African (Sudanese or Berber) blood, as is also stated by BERTHOLON and CHANTRE themselves, who (l.c. p. 277) believe that "les Carthaginois regardés comme phéniciens ont 77 comme indice cephalique" (males and females together apparently). The average index in the population of Carthage was apparently lowered by dolichocephalic mixtures.

The paper describing Phoenician skulls found in France by MARICHARD and PRUNER BEY<sup>3)</sup> was not at my disposal.

So the two Phoenician skulls found in Sardegna and described by MANTEGAZZA and ZANNETTI<sup>4)</sup> had a higher index (76.97 for the presumed female, and 78.02 for the presumed young male<sup>5)</sup>).

Phoenician skulls from Phoenicia itself hitherto have been only described by CHANTRE<sup>6)</sup>, who examined crania collected by HAMDY BEY at Sidon (now Saida). These skulls dated from the V<sup>th</sup> to IV<sup>th</sup> century. They are now at the Museum in Constantinople. Six skulls were found by HAMDY BEY. The skull of the Sidonian king TABNITH had an index of 77.12, a female skull (perhaps of his wife) 84.23. Three more male skulls found in Phoenician

<sup>1)</sup> "Sexe probable féminin" see BERTHOLON: Deux crânes phéniciens trouvés en Tunisie. *l'Anthropologie*, Paris, 1890, p. 314.

<sup>2)</sup> BERTHOLON et CHANTRE. *Recherches anthropologiques dans la Berberie orientale*, Lyon, 1913. (see also BERTHOLON: Documents anthropologiques sur les Phéniciens *Bull. de la Soc. d'Anthrop. de Lyon*, 1892, Tome XI, p. 179; the same: *Identités des caractères des Basques et des Phéniciens*. *Bull. de la Soc. d'Anthrop. de Paris*, 1896.

<sup>3)</sup> MARICHARD et PRUNER BEY. *Les Carthaginois en France*. Montpellier, 1870.

<sup>4)</sup> MANTEGAZZA e ZANNETTI. Note antropologica sulla Sardegna. *Archivio per l'Antrop. e l'Etnol.*, Tomo VI, 1876, p. 17. These authors refer to a third skull found on Sardegna and described by NICOLUCCI. I was not able to obtain NICOLUCCI's paper (*Un antico cranio rinvenuto in Sardegna*. Torino, 1863), but it seems to me that the skull figured by MANTEGAZZA and ZANNETTI as a Sardinian skull may be just as well Phenician.

<sup>5)</sup> The sex determination seems very doubtful. It might be just as well the reverse. This would give a young male index of 76.97 and an adult female index of 78.02, being the same as with my skulls.

<sup>6)</sup> CHANTRE. Crânes de la nécropole de Sidon. *Bull. de la Soc. d'Anthrop. de Lyon* 1894. Tome 13. p. 12. — The scattered skulls HAMDY BEY found at Saida (ind. 82.5) probably are no ancient Phoenician skulls. Also to day an index of 82.5 is not so rare at Saida.

sarcophagi had an index of 76.75 ; 76.96 and 77.26. Finally a beautiful Greek sarcophagus (the so called sarcophagus of Alexander) contained a male skull of 86.11. As at that time the Greek and other peoples were quite influential on the coast, I am inclined to believe that the latter skull was not Phoenician nor the female skull. This would give a male Phoenician skull index = 77.02.

My own researches on Phoenician skulls from Phenicia concerned one male skull from Byblos (Djebail), found in a Phoenician tomb of the 13<sup>th</sup> century B.C. and 15 skulls from a necropolis at Sidon (Saida) dating from the 5<sup>th</sup>—4<sup>th</sup> century B.C.

The skulls from Sidon were collected by the late American missionary Mr. FORD. After his death the collection was presented to the National Museum at Beirut where I was allowed to measure and photograph them in June 1930, shortly after their arrival.

The oldest skull — the one from Byblos — a male skull — is reproduced on Plate I. Its measurements and indices are as follows :

Name	length	width	height	l. w. i.	w. h. i.	l. h. i.
Phoen. 13th cent. Byblos	19.2	14.6	12.2	76.04	83.56	63.5

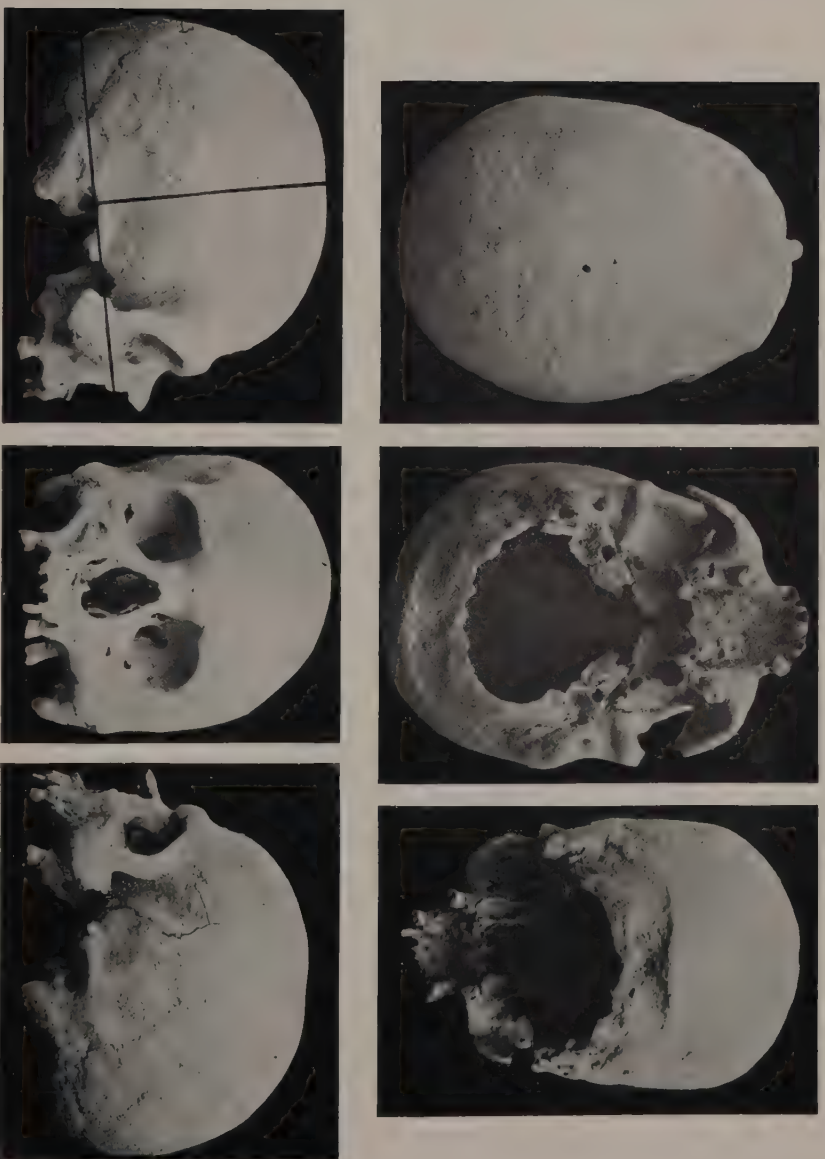
Further characteristics of this slightly platycephalic skull are : "occiput en chignon" (a racial peculiarity to be observed even in some Phoenician statuettes), the relation of the postauricular length of the skull to the total skull length being 0.49 ; aquiline nose (also to be observed in Phoenician statuettes and with the sculptures of the wailing women on Phoenician tombs), nasal index 50.6, rectangular orbits, well developed supraorbital ridges, protruding specially laterally. The development of the jugae is not as strong as might seem on first sight, the minimum frontal width being small (the min. front. width-jugular index is 76.2).

The base of the skull is damaged so that the exact relations of the foramen magnum cannot be controled. As, however, the occipital condyles are preserved the distance between them and the inion may be estimated and confirms the large occipital development. Palato-alveolar (Gaumen) index 90.

We probably have to take this as a good example of a typical male Phoenician skull, a supposition confirmed by studying the Phoenician skulls from Sidon (Saida).

Of the 22 sarcophagi collected at Saida by Mr. FORD and sent to Beirut, seven belonged to males, 15 to females. Of the 15 female sarcophagi three were either empty or the calvarium was so damaged that no measurements could be taken. Four other sarcophagi contained skulls of an index 86.7 (N<sup>o</sup>. III) ; 84.7 (N<sup>o</sup>. VII ♀) ; 85.2 (N<sup>o</sup>. XI), and again 84.7 (N<sup>o</sup>. XIV <sup>1</sup>).

<sup>1</sup>) The Roman figures between brackets indicate the cipher I put on the skulls.

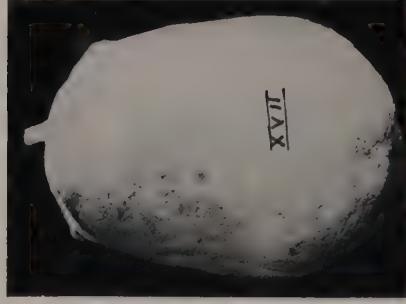
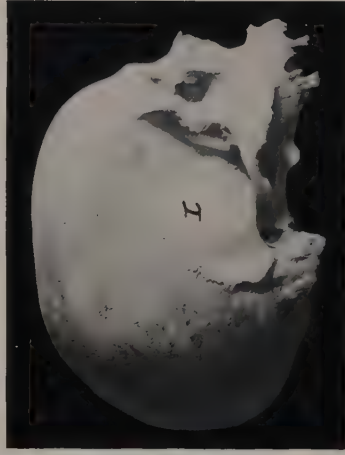
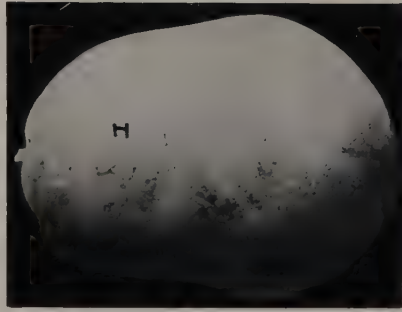


Phoenician skull from a sarcophagus at Byblos (Deball), 13th cent B.C.









Phoenician skulls from sarcophagi at Sidon.

These skulls (see also HAMDY BEY's collection) apparently were either not Phoenician or had a type that cannot be considered as typical for the race (further one of them — N<sup>0</sup>. III — was artificially compressed in the parietal region on both sides). Leaving these skulls out of consideration the remaining male skulls had the following measurements and indices.

Males	length	width	height	l. w. i.	w. h. i.	l. h. i.
No. I . . . . .	20.0	15.0	12.3	75.00	82.00	61.50
No. II . . . . .	19.1	14.4	12.2	75.40	84.70	63.87
No. V <sup>1)</sup> . . . . .	18.5	13.7	11.6	74.05	84.67	62.70
No. VI . . . . .	19.2	14.7	12.0	76.56	81.63	62.50
No. XIII . . . . .	19.15	15.1	12.4	78.85	82.12	64.75
No. XII . . . . .	19.8	14.9	11.5	75.25	77.20	58.10
No. XV. . . . .	19.0	14.7	11.3	77.37	76.87	59.47
Average . . . . .	19.25	14.65	11.96	76.07	81.31	61.84

The female measurements and indices were as follows:

Females	length	width	height	l. w. i.	w. h. i.	l. h. i.
No. IV . . . . .	18.6	14.5	11.5	77.96	79.30	61.80
No. VIII . . . . .	16.9	13.4	11.2	79.29	83.60	66.30
No. IX . . . . .	18.7	14.0	11.2	74.87	80.0	60.0
No. X . . . . .	17.9	14.1	11.5	78.77	81.56	64.25
No. XVI . . . . .	17.8	14.3	11.8	80.34	82.52	66.30
No. XVII . . . . .	18.9	14.5	11.7	76.72	80.69	61.90
No. XVIII . . . . .	17.4	13.8	11.9	79.31	86.23	67.24
No. XIX . . . . .	17.7	14.0	11.3	79.10	80.71	63.84
Average . . . . .	17.99	14.07	11.51	78.29	81.83	63.95

From this it appears that the indices of the male Sidonian skulls agree very well with those of the Byblos skull, while — as is usual with mesocephalic races — the female index (corresponding with the female index found by MANTEGAZZA and ZANNETTI) is higher, the sexual difference being 2.22 in favor of the female. Taking into consideration also the four male Sidonian skulls described by CHANTRE and my Byblos skull

<sup>1)</sup> This probably was a young individual.

the male index is 76.4, giving a sexual difference of 1.89. The similarity of the Sidon skulls with the Byblos skull appears also from the other indices I took (see also plate II and III).

Names	min. front. jug. ind.	nasal ind.	pal. alv. ind.	post. auric. ind.
Byblos ♂	76.2	50.6	90	49 .
Sidon ♂	79.2	49.8	93	51

In addition to these skulls I have been able to measure and photograph two skulls or parts of skulls present in the Museum at Palmyra (oasis Thadmor).

Palmyrene skulls have been studied before by C. CARTER BLAKE<sup>1)</sup> who examined the human remains derived from Palmyra in 1872 by Captain BURTON. These remains belonged to eight individuals. Of five of them only pieces of calvaria were found. Of three others (Nos 2, 3 and 4 of the BURTON collection) No. 2 and 3 had characteristics that forcibly reminded BURTON and BLAKE of the Phenician skull figured on Plate II of MARICHARDS and PRUNER BEYS paper (l.c. supra). Their measurements and indices were as follows :

BURTON's skulls	length	width	height	l. w. i.	w. h. i.	l. h. i.
Palm. No. 2 . . .	20.8	14.6	12.4	70.2	84.9	59
Palm. No. 3 <sup>2)</sup> . . .	17.1	13.1	11.1	76.61	84.7	64

In 1875 BUSK<sup>3)</sup> described three other skulls collected at Palmyra by Mr. COTESWORTH :

Cotesworth's skulls	length	width	height	l. w. i.	w. h. i.	l. h. i.
Palm. No. I . . .	6.9 i.	5.4 i. <sub>2</sub>	5.2 i. <sup>4)</sup>	78.26	(96.3) <sup>4)</sup>	(75) <sup>4)</sup>
Palm. No. II . . .	7.6 i.	5.6 i.	5.7 i.	73.68	(98.2)	(75)
Palm. No. III . . .	7.6 i.	5.4 i.	5.5 i.	71.05	(102.0)	(72)
Average l. w. i. . .				73.96		

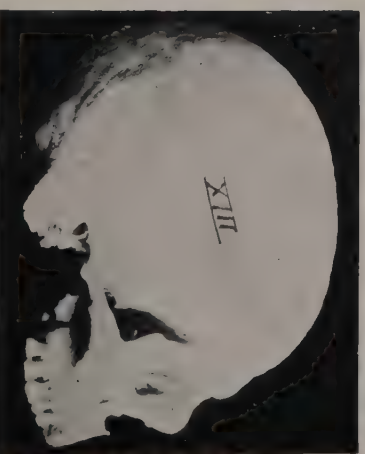
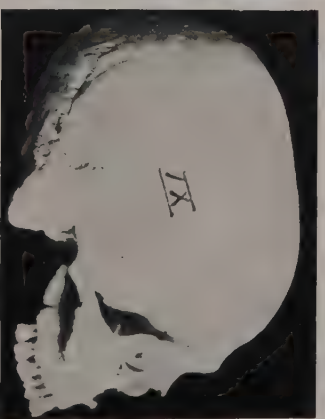
<sup>1)</sup> C. C. BLAKE. Notes on human remains from Palmyra. Journ. of the Anthropol. Instit. of Gr. Brit. and Irel. Vol. I, 1872, p. 312.

<sup>2)</sup> This skull is reproduced in SELIGMAN's paper (l.c. infra).

<sup>3)</sup> BUSK. Notes on some skulls from Palmyra, presented to the institute by the late Mr. COTESWORTH. Journ. of the Anthropol. Instit. Vol. IV, 1875, p. 366.

<sup>4)</sup> I do not know how this height was measured, the height indices being so different from mine.

C. U. ARIËNS KAPPERS: CONTRIBUTIONS TO THE ANTHROPOLOGY OF THE NEAR-EAST. III.      PLATE III.

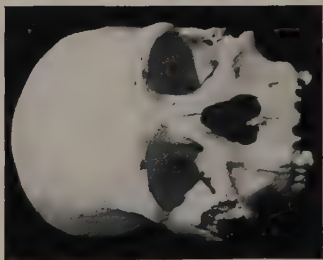
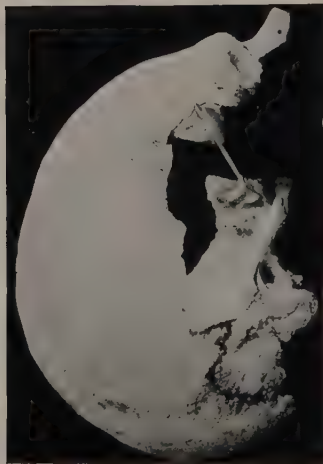
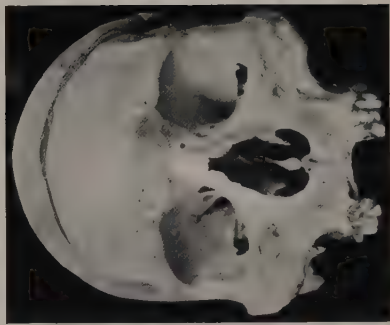
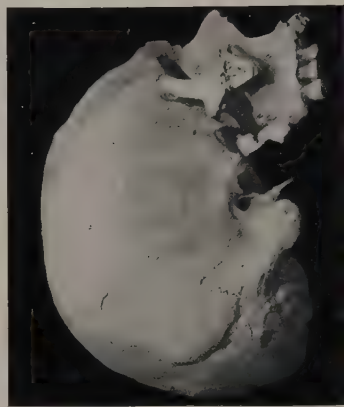
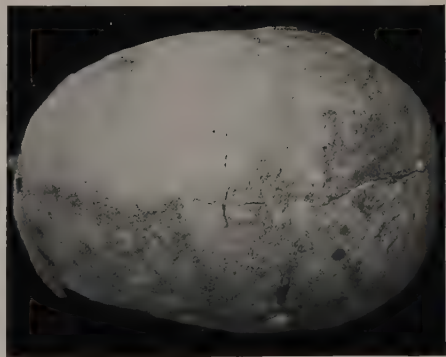


Phoenician skulls from sarcophagi at Sidon.









Skull of Father Bergy.

Palmyrene skull.

Recent Arab Semitic skull.

The average l.w.i. of the BURTON and the COTESWORTH skulls is 73.96 (74). Later some more skulls were sent by Captain BURTON to the Anthropological Institute in London but OWEN says practically nothing about them in his report<sup>1)</sup> on this subject, except that they resemble Egyptian skulls, he described.

The Palmyrene skulls I studied in Palmyra were not complete. Of one, according to its size, a male one, only the right lateral half was complete, of the other one only the frontal part was well preserved (c.f. Plate IV).

According to the custodian both were found in the Palmyrene tomb towers<sup>2)</sup>, wellknown to visitors of this place and dating from the 2<sup>nd</sup> and 3<sup>d</sup> century A.D. — Here I give the measurements and indices of the sagittomedially halved skull comparing them with the male Byblos and the average of the male Sidon Phoenician skulls :

Name	length	width	height	l. w. i.	w. h. i.	l. h. i.
Byblos . . . . .	19.2	14.6	12.2	76.04	83.56	63.5
Sidon . . . . .	19.25	14.65	11.96	76.07	81.31	61.84
Palmyra . . . . .	19.1	14.6	11.8	76.40	80.82	61.78

The relation of the postauricular length to the total length of my Palmyra skull was 0.52 (0.47 in BURTONS skull N<sup>o</sup>. 2). In the other, frontal half, the nasal index was 50.0 (in BURTONS N<sup>o</sup>. 2 : 47.0), the minimum fronto-jugular index was 80 in my skull (72 in BURTONS N<sup>o</sup>. 2) Comparing these data with those of my Phoenician skulls we find :

Name	min. front. jug. ind.	nasal ind.	palat. index	post. aur. length i.
Byblos . . .	76.2	50.6	90	49
Sidon . . .	79.2	49.8	93	51
Palmyra . .	80.0	50.0	?	52

We see that these indices as well as the l.w.i., the w.h.i. and l.h.i. of the Byblos, Sidon and Palmyra skulls resemble each other very much. Other points of resemblance are platycephaly<sup>3)</sup> "occiput en chignon", rectangular orbits, distinct supraorbital ridges and high palate.

<sup>1)</sup> OWEN. Observation on the collection of skulls sent by Capt. BURTON in Sept. 1878. Journ. of the Anthrop. Instit. of Gr. Britain and Irel. Vol. VIII, 1879, p. 323.

<sup>2)</sup> For a description of these tomb-towers see COTESWORTH. Journ. of the Anthrop. Instit. of Gr. Brit. and Irel. Vol. IV, 1875, p. 364. One of them shows the year 414 written in Greek and Aramean, i.e. about 102 A. D. (COTESWORTH).

<sup>3)</sup> The platycephaly referred to in this paper is the platycephaly as seen in the sagittal aspect (cf. Plates I, II, III).

Taking everything together there can be no doubt concerning the close relationship of the Phenician population B.C. with the Palmyrene Arameans (the inscriptions on the tombs in Palmyra are mostly in Aramean), at the beginning of the Christian era.

Before dealing with the question of the present representatives of this race I want to say a few words concerning two other old skulls, one found by Father BERGY of the Université St. Joseph at Beirut in a riverbed of the Beká (the valley between the Lebanon and Antilebanon). Unhappily this skull was badly damaged on its voyage from France where Father BERGY sent it for Mr. BOULES opinion about it. After its restoration by Father BERGY it had an index of about 70, slight supraorbital ridges and a pronounced aquiline nose. Its postauricular-total length index is 47.1, the minimum front jugular index somewhat less than 81. Although its frontbones are slightly more receding, I quite agree with Father BERGY (and so did Mr. BOULE) that this is a protosemitic skull.

It certainly belongs to the same type of people as mentioned above. The other skull to be mentioned here is a Nabathean (southern Sinaitic) skull described by BUSK<sup>1</sup>). Its indices are l.w.i. 72, w.h.i. 81.8, l.h.i. 60.0. Its min. front jugular index 82.6, nasal index 50, postauricular length index also 50. So also this skull bears all the characteristics mentioned above.

Referring for the Megiddo skulls to my next paper, I now come to the question: who are the present representatives of this race?

In order to remain in the same field of information I shall first give the measurements and indices of a recent skull present in the anatomical Institute of the American University of Beirut. Unhappily its origin is unknown but it bears most characteristics of the skulls just described. It possibly originates from one of the Hauran Arabs frequently working in Beirut.

It certainly is an Arabic Semitic (not a Lebanese) skull. I give its measurements and indices together with those of the Sinai Arab skull of the Royal College of Surgeons N<sup>o</sup>. 624, mentioned in SELIGMANS<sup>2</sup>) excellent paper on the physical characters of the Arabs.

Names	length	width	height	l. w. i.	w. h. i.	l. h. i.
Rec. Sem. . . . .	18.4	13.5	11.4	73.4	84.4	62
R. C. S. 624 . . . .	18.2	13.4	13.4 <sup>3</sup> )	73.6	—	—

<sup>1</sup>) BUSK. Description a Nabathean skull. Journ. of the Anthropol. Instit. of Gr. Brit. and Irel. Vol. VIII, 1879, p. 321.

<sup>2</sup>) SELIGMAN. Journ. of the Anthropol. Instit. of Gr. Brit. and Irel., Vol. 47, 1917, p. 234.

<sup>3</sup>) While my height measures of the skull were taken in the Frankfurt horizontal. perpendicular on the upper edge of the meatus auditorius externus I suppose that SELIGMAN's height measure was taken in a different way and that his height indices and mine are not comparable (see also footnote 4 on the preceding page).

Some other indices of my recent skull are :

Name	min. front. jug. i.	nasal ind.	palatal. ind.	postauric. length i.
Recent semite	78	48.1	?	43

All these indices agree quite well with the Phoenico-Palmyrene indices mentioned above. Only the postauricular length index is slightly smaller (the same postauricular length index, however, occurs with the Midian Arab skull, R. C. S. N<sup>o</sup>. 623 figured by SELIGMAN l.c. Plate IX).

Also the skulls of Beduins from Tripolis studied by MOCHI<sup>1)</sup> and GIOVANOZZI's second group, the Taura Arabs<sup>2)</sup>, show a similar form and indices. So I can confirm SELIGMAN's statement that the Adnan Arabs, the Beduin tribes of North Arabia (including the Syrian desert) are the living relatives of the bearers of those Palmyrene skulls and I may add to it that their older representatives were the Phoenicians. As not so many head measurements and indices of Syrian and Egyptian Adnan Arabs are given in literature I finish with giving those of 107 Beduin and 117 Egyptian Arab males.

Names	length	width	height	l. w. i.	w. h. i.	l. h. i.
Syrian Beduins . . .	18.71	14.38	12.7 <sup>2)</sup>	76.85	88.3 <sup>2)</sup>	67.9 <sup>3)</sup>
Egypt. Arabs . . .	19.04	14.45	13.0 <sup>2)</sup>	75.89	90.1 <sup>2)</sup>	68.4 <sup>3)</sup>

With the probability calculation the index of 101 Beduins of the Syrian desert is 77.2 ( $\pm 0.97$ ), with a variations spread ( $\sigma$ ) of 3.24.

Considering the fact that the l.w.i. index on the head — according to R. MARTIN<sup>4)</sup> — is about one higher than on the skull (76, see above) makes the resemblance of the Beduin indices with the Phoenician male index still more striking.

Personally I measured no Beduin women but it would be interesting to know if also here as with the Phoenicians (and with the Samaritans, see my next paper) the female index is also about two higher than the male.

<sup>1)</sup> MOCHI. Presentazione di crani d'indigeni di Tripolis. Archivio per l'Antrop. e l'Etnol., Tomo 42, 1912, p. 381. *The same*: Sull'antropologia degli Arabi. Ibidem Tomo 37, 1907, p. 411, see specially his Tav. VIII and X.

<sup>2)</sup> GIOVANOZZI. Cranii arabi del museo antropologico di Firenze. Arch. per l'Antrop. e l'Etnol. Tomo 34, 1904, p. 343, (especially skull 4353, p. 352).

<sup>3)</sup> That all the figures concerning the height of the head measured on the living are higher than those on the skull is due to the fact that the tragion (incisura auricularis anterior) lies lower than the upper edge of the meatus audit. extern. used in my skull measurements.

<sup>4)</sup> R. MARTIN. Lehrbuch der Anthropologie, p. 198.



That with the Arabs of Egypt this index is lower <sup>1)</sup> may be due to some admixtures with African tribes (Sudanese or Berbers, see above).

In fig. 1 the crossed curve shows the indices of my Beduins of Syria, the dotted curve all the Byblos, Sidonian and Palmyrene indices hitherto

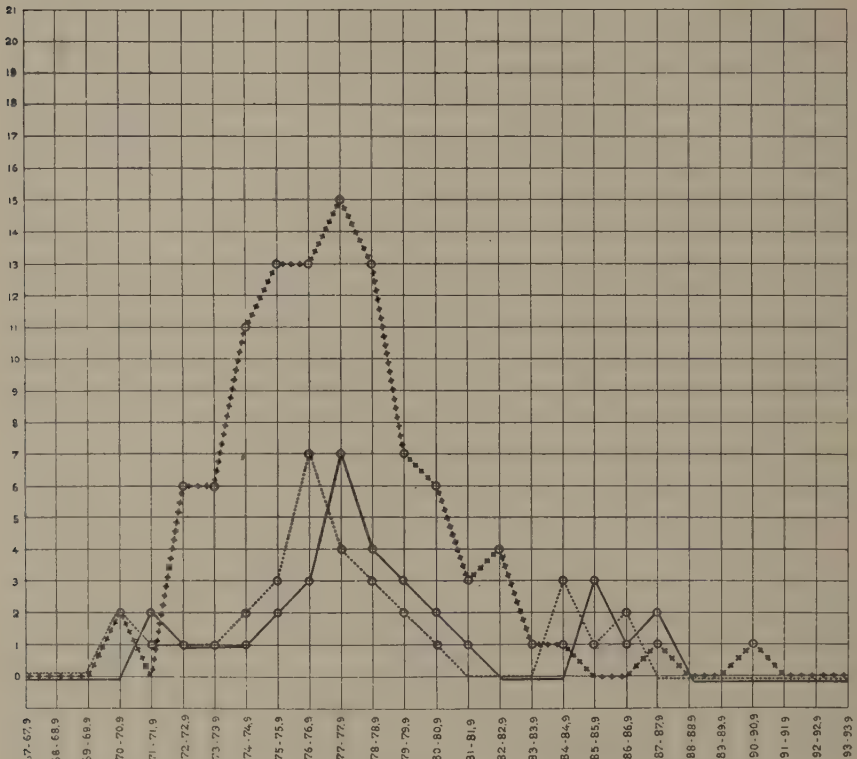


Fig. 1.

Crossed curve = Syrian Beduins; dotted curve = Phoenician skulls from Phoenicia (Sidon and Byblos), and Palmyrene skulls; continuous curve = the head indices corresponding to the latter (pure Phoenician: 77—77.9).

available. Parallel to the latter but one figure more to the right runs the curve, indicating the head indices of the bearers of these skulls (these indices being one figure higher than the skull index). From the latter it appears that its highest elevation coincides exactly with the Beduin top.

In fig. 2 I plotted the head indices of my 117 Egyptian Arabs, to which I added the indices of all the Carthaginian skulls described by BERTHOLON and CHANTRE, again adding the one point higher head curve of those

<sup>1)</sup> As quoted in my second contribution CHANTRE (*Recherches anthropologiques en Egypte*, p. 196), found still somewhat lower indices with the Aulad Ali of the Delta (average 75.37) and with the Arabs round Lake Menzaleh (74.48). — In the Fayum district the indices are still lower (72.82).

Carthaginians. Of the latter curve a large part runs parallel to my African Arab curve. In addition it shows, however, another high top, corresponding exactly with the Syrian Beduin or real Phoenician top (77—77.9).

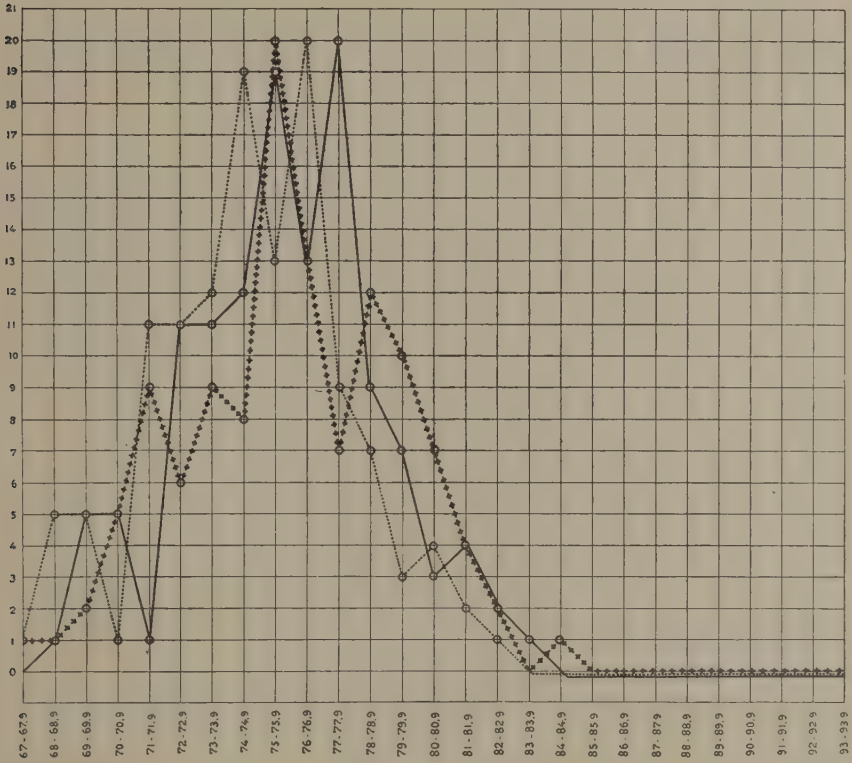


Fig. 2.

Crossed curve = African (Egyptian) Arabs; dotted curve = Carthaginian skulls described by BERTHOLON and CHANTRE; continuous curve = the head indices corresponding to the latter (note the pure Phoenician top at 77—77.9).

**Anthropology.** — *Contributions to the Anthropology of the Near-East.*  
N<sup>o</sup>. IV. The Semitic Races. By C. U. ARIËNS KAPPERS.

(Communicated at the meeting of January 31, 1931).

For my studies on the Semitic races in the Near-East I measured the heads of 107 male individuals of more or less nomadic tribes of the North Syrian desert, Beduins from the surroundings of Palmyra, Aleppo, Selemiye, and some originating from Deirel Zore, whom I met in Aleppo, and from the Hauran district (Beni-Darra). In addition I measured some Arabs from the Hedjaz, Nedjd and Bahrein (in the Persian Gulf).

Of the Arabs from Egypt (chiefly lower Egypt) I measured 117 male individuals and of the Arabs of Palestine (north of the line Jaffa—Jericho) 139 males. Altogether 363 Arab Semites.

Of another group, of Semites which I called "the desert border population", already referred to in my second article (the population of Aleppo, Hama, Homs, Ma'alullah and Damascus) 135 males were measured. The same top index being shown by about 20 % of the Mesopotamian population (22 individuals) and by 15 % of the Lebanese and Be'ka population makes the total number of the desert border population measured 188.

Of the Hebrew Semites I measured 84 Samaritans of Nablus. I want to express my thanks to Mr. KEMAL KHOURY from Nablus who helped me as a guide and interpreter in the Samaritan colony. In addition I measured 101 Sephardim from Amsterdam (74), Syria, Palestine and Bagdad (27) and 100 Aschkenasim (74 from Amsterdam, 26 from Palestine and Syria). In addition I measured 65 adult males of Sephardim-Aschkenasim offspring, together 350 Hebrew Semites, making the total of the Semites measured 901.

Besides I had the opportunity to measure two Hebrew skulls of Solomons time (10<sup>th</sup> century B. C.) found with the excavation of Megiddo<sup>1</sup>).

I am much indebted to the representatives of Mr. P. L. O. GUY of the Oriental Institute of Chicago, for this permission.

As already stated in my third contribution the average indices of the male Beduins and Arabs of Syria were l. w. i. 77.21, (according to the probability calculation,  $\pm 0.97$ ), w. h. h. 88.3; l. h. i. 67.9. The average

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<sup>1</sup>) As these skulls were from a tomb (N<sup>o</sup> 232 of the excavation) in Megiddo itself, they were at all probability Hebrew skulls.

measures and indices of the 117 Egyptian Arabs differ but little. Their length and height is slightly larger.

TABLE I.

Groups	length	width	height	l. w. i.	w. h. i.	l. h. i.
Syr. Beduins . . . .	18.71	14.38	12.7	77.2	88.3	67.1
Egyp. Arabs . . . .	19.04	14.45	13.03	75.89	90.1	68.43

From the frequency curves in figure 1 it appears that the (strong) curve of my Egyptian Arabs runs largely parallel to the (thin) Beduin curve as far as concerns the l. w. i. indices. There is however a group among the Egyptian Arabs at 71—71.9 that practically fails in the Beduins and probably is due to an admixture of African blood (Sudanese or Berber) which may also explain the slightly lower average index (75.89) of my African Arabs in comparison with the Syrian Beduins.

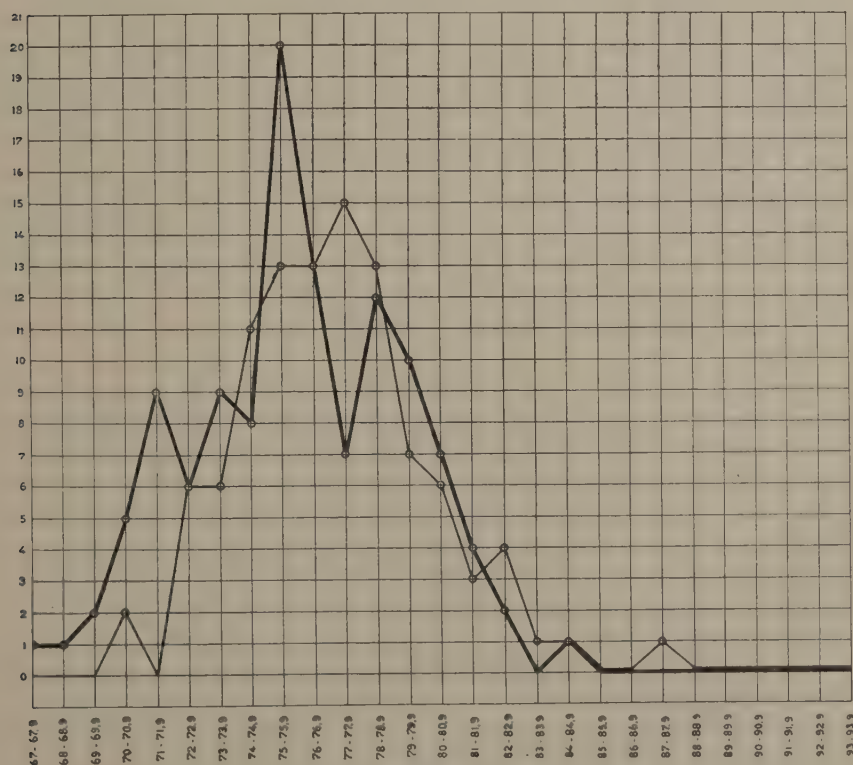


Fig. 1.

Strong line = Egyptian Arabs; thin line = Beduins of Syria.

Superposing on these curves the indices of the Phoenician skulls hitherto found in Phoenicia itself, including the Palmyrene skulls, and adding one cipher for the difference in skull and headindex it appeared that the Phoenician curve runs parallel to the Beduin Arab curve so that there is no doubt concerning the Phoenico-Palmyrene character of the latter (see my third contribution).

A comparison, however, of the present Egyptian Arab curve with the Carthagene curve shows the fact already referred to in my third contribution that those Carthagenes were slightly mixed with a more dolichocephalic race, but less so than the present Egyptian Arabs, there being still a typical 77 top among the Carthagenes.

The question, however, arises are these Arab groups the only relatives of that Phoenician stock in the Near-East and what about the Samaritans and the Eastern Jews?

Of the Samaritans only a small group is left, living at Nablus near the ruins of Samaria and Szichem. Since centuries they only marry amongst themselves. Only one marriage with a Jewess is stated recently by SZPIDBAUM.

They have been studied somatically by HUXLEY <sup>1)</sup>, WEISSENBERG <sup>2)</sup>, SZPIDBAUM <sup>3)</sup> and myself, while HIRSZFELD and PARR (see below) tested their bloodtypes. HUXLEY measured 35 males and found an average index of 78.1, WEISSENBERG, who only measured 20 males found an average index of 76.2. SZPIDBAUM, who measured 94 individuals found an average l. w. i. of 77.64 with the males and of 80.84 with the females.

Personally I measured 84 individuals, 27 adult men, 32 adult women and 25 children of both sexes. With the adult males I found an average l. w. i. of 77.23; with the females, 78.97, while the average of the children was 78.27.

The measurements and indices are as follows:

TABLE II.

Groups	length	width	height	l. w. i.	w. h. i.	l. h. i.
Sam. adult ♂ . . .	19.11	14.76	13.36	77.23	90.52	70.0
Sam. adult ♀ . . .	18.02	14.23	12.57	78.97	88.30	69.76
Sam. childr. ♂ and ♀	17.53	13.72	12.53	78.27	91.33	71.47

1) HUXLEY. Zur Anthropologie der Samaritaner. Zeitschr. f. Demographie und Statistik der Juden. 1906. p. 137.

2) WEISSENBERG. Die autochtone Bevölkerung Palästina's in anthropologischer Beziehung. Ibidem, Jahrg. V. 1909. p. 129.

3) SZPIDBAUM. Die Samaritaner. Mitteil. aus der Anthropol. Gesellsch. in Wien. Bnd. 57, p. 130, 1927.



Superposing the total <sup>1)</sup> Samaritan curve on the curve of my Beduins (fig. 2) we see that the main group of the Samaritans runs exactly parallel to the Beduins and that those that fall outside the main frequency curve

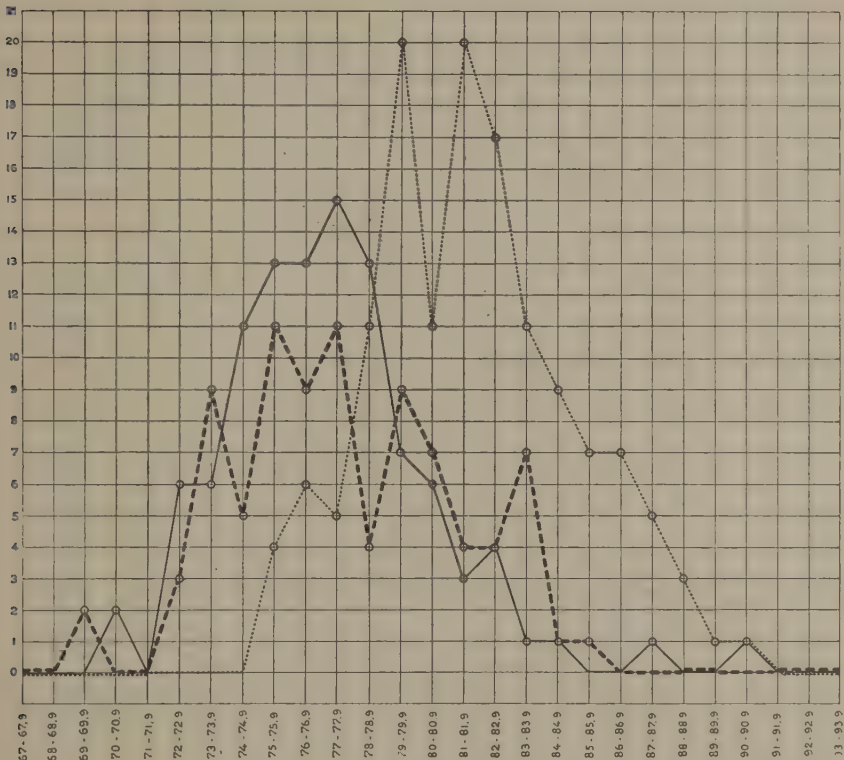


Fig. 2.

Thin continuous line = Beduins; dotted line Palestinian Arabs; broken line = Samaritans.

of the latter fall so far to the right that they probably do not belong to the same group. So the Samaritans probably are a mixture of Jews with another race. Which is this race? Leaving those Samaritans that have an index of 81—81.9 and more (5 adult males and 6 females) out of consideration in establishing the character of the adult main group, this main group (80 % of the population) would have an average l.w.i. of 75.94 for the males, 78.05 for the females, thus showing clearly the Phoenician type also in this respect that with both, the Samaritans and the Phoenicians, the sexual difference in the l. w. i. is about 2 (2.22 with the Phoenicians 2.11 with the Samaritans) in favor of the female.

<sup>1)</sup> As the Beduins with whom I compare here the Samaritans are only male Beduins, only the male Samaritan curve should be compared with theirs. The number of my males (children included) being however only 42, this figure is too small to give a speaking curve. So I prefer to superpose the total Samaritan curve on the male Beduin curve.

Also the acquiline nose, the occiput en chignon and the relation between the minimum front- and jugular width with several male Samaritans gave an analogous impression, even without exactly measuring these indices <sup>1)</sup>.



Fig. 3. Thin line = Sephardim; strong line = Aschkenasim.

My Jewish frequency curves were so made that I plotted the adult male Sephardim (thin line) and Aschkenasim (strong line) together (fig. 3).

From this it appears that the Sephardim have two tops, the highest at 77—78, a smaller one at 80—82.9 and that the latter top coincides with my Aschkenasim, the majority of which have an index of 81.

From the same curves appears that with the Sephardim a good many have various lower indices than 77. On the other hand with the Aschkenasim the opposite is seen, there being a good many with higher indices.

<sup>1)</sup> The fact that the racial blood index of the Adnan Arabs is 1.59 while that of the Samaritans, tested by PARR (84 individuals) is 2.35 may perhaps be explained by the exquisite inbreeding in this group, which may cause the B component to keep the Aschkenasim type (see below).

Still the fact that both groups of Jews have a top 80—82.9 in common coincides strikingly with the relations I found with the two skulls from Solomons time found at Megiddo. The measurements and indices of these skulls were :

TABLE III.

Names	length	width	height	l. w. i.	w. h. i.	l. h. i.
No. 1 . . . . .	18.6	14.8	12.1	79.57	81.76	65.05
No. 2 <sup>1)</sup> . . . . .	18.8?	15.3	12.3	81.38	80.39	65.43
Average. . . . .	18.7	15.05	12.2	80.45	81.58	65.24

If both these skulls are of males (about which I could not obtain certainty) they would suggest that the *original male Hebrew index* may have been about 80.5 on the skull, i.e. about 81.5<sup>2)</sup> on the head<sup>3)</sup> with variations, at least between 80.6 and 82.4, probably between 79 and 83.5 or so.

In connection herewith it is striking that the present Arab population of Palestine North of the line Jaffa—Jericho, just as the Arabic population of the desert border East of the Lebanon have an index distinctly higher than the Adnan Arabs or Phoenico—Palmyrene group, The figures I found for the Palestinian Arabs differ from those found by WEISSENBERG, (l.c. supra).

WEISSENBERG measured 62 Palestinian Fellaheen, 30 from Safed in the North of Palestine and 32 from Rishon el Zion near Jaffa. With the former he found an index of 75.7, with the latter (near Jaffa) 76.9. I am, however, convinced that if he had measured more Arabs, North of the Jaffa—Jericho line he would have found a higher index. I found WEISSENBERG's index at Ghaza.

The frequency curve of 139 males North of the line Jaffa—Jericho (see fig. 4) only shows a small quantity of the typical Adnan index (76—77), the highest tops being at 79—79.9 and at 81—81.9. Further at the right of the curve appear a few tops that may result from Hittite (Armenoid) or other admixtures (see below).

If we consider the separation of these highest tops as incidental, 79.9 being very near 81, the mean of these tops (80—80.9) coincides exactly

1) With this skull the glabella was broken, so that the length could be only estimated, the eye ridges being present.

2) It is interesting that DUDLEY BUXTON in his peoples of Asia estimates the average index of the Jewish people to be 81 (p. 97). One can however hardly speak of an average index as the number of Sephardim is related to the Aschkenasim as 80 % to 92 %.

3) R. MARTIN, *Lehrbuch der Anthropologie*, p. 198.

with the top of the desert border population the average of which according to the probability calculation is 81.7 ( $\pm 0.99$ ).

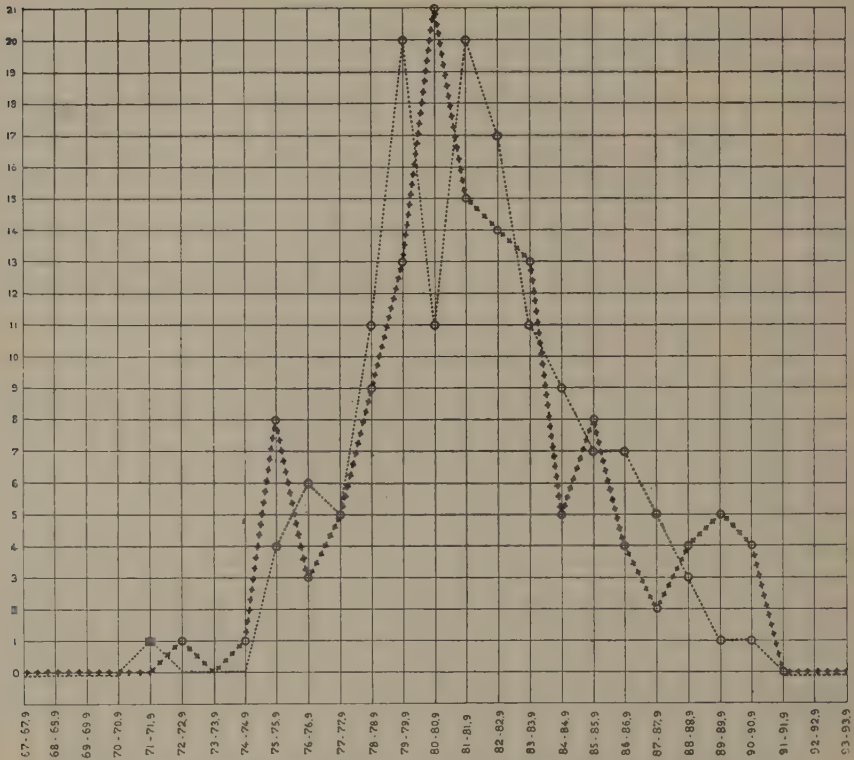


Fig. 4. Crossed line === desert border population; dotted line Palestinian Arabs.

This comes very near to what might perhaps be the original Hebrew index. So the question arises if here we have not to do with racial relatives of the non-Phoenician population of Palestine, that are not to be considered as Jews, but that are racially connected with "Chebiru", and may have been partly included in the so called ten Northern tribes, at least in the empire of Saul, David and Solomon which extended far North along the Lebanon — on the desert border up to Aleppo and Palmyra.

One has to be very careful here, as some historians believe that the Northern Hebrews have been entirely annihilated (cf. AUERBACH, l.c. infra). But perhaps they have been chiefly annihilated as a Jewish sect.

An average index 81.7 (and also that Northern Palestinian top of 81—81.9) being much too high to belong to the Adnan Arabs and too low to indicate Kohtan Arabs (Hittite blood) it seems at least possible — especially if my assumption, that the original Hebrew index was about 80.5—82.5 is right — that we have to do here either with remains of the "ten Northern Hebrew tribes" or with "Chebiru" influence in general. This

possibility increases if we consider the spread of this index, so outstanding in my curves that it must have a racial significance.

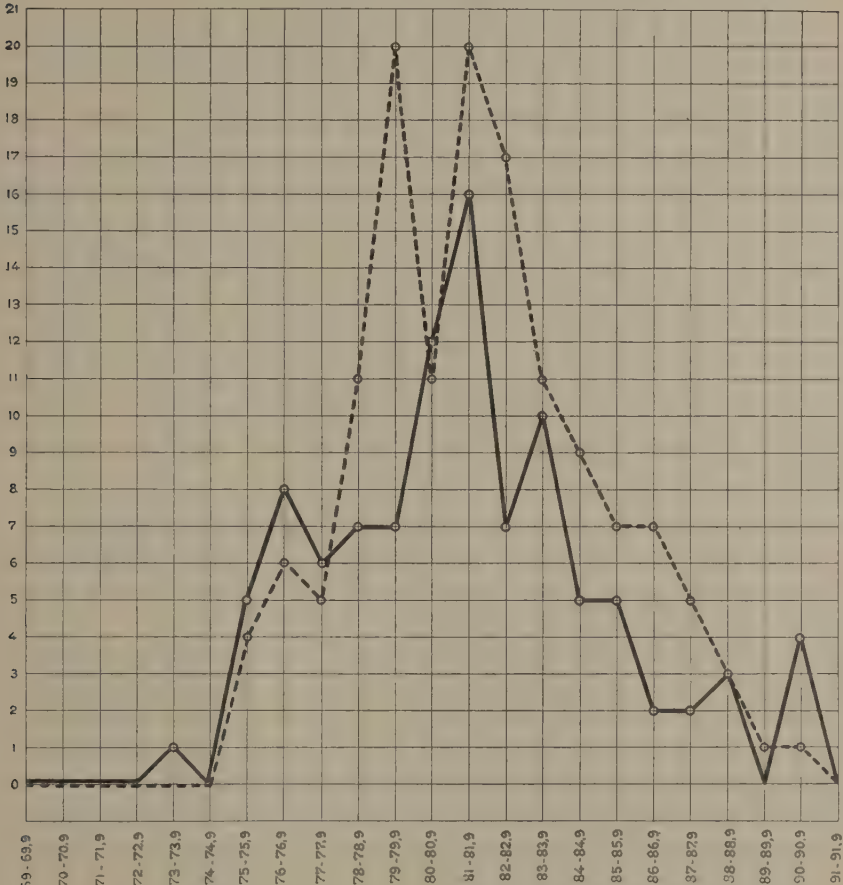


Fig. 5. Broken line = Palestinian Arabs; strong continuous line = Aschkenasim.

As stated before, this index is by far the prevailing one in North-Palestine and in the desert border cities from Damascus<sup>1)</sup> to Aleppo<sup>2)</sup>. The same top returns most distinctly with 15 % of the Lebanese population (see my second contribution, table IV), but practically fails nearer the coast North of Tripolis (Tripolis, Safitah, Bishraye, exquisite Hittite sites). On the eastern border of the Syrian desert — the old Assyrian

<sup>1)</sup> According to WEISSENBERG (l.c.) the Jewish index in Damascus is still 80.9 which he believes to come near the old Jewish index that according to him was but slightly lower.

<sup>2)</sup> According to BERNARD old Jewish colonies still exist in the desert border cities (des communautés anciennes existent à Alep, Hama, Homs, Damas). *Annales de Géographie*, Tome 28, 1919: La Syrie et les Syriens, p. 45). The same is stated already in the 12th century by Benj. of Tudela.



and Babylonian countries — it returns with 20 % in my curves (see the Irakkian curve in Table III of my second contribution).

A spread of Hebrew tribes (especially of those of the kingdom of Israël) in this direction might be explained by the fact that they were living in constant enmity with the Southern Jews (the kingdom of Juda) and also by the fact that Sargon of Assyria took a great many of them to Assur (Northern Mesopotamia: the Assyrian exile; 720 B. C.).

Another possibility, perhaps the first, to be considered here is that this group is related to the population of Palestine and Syria before the Hebrew invasion, specially the *Amorites*, who, coming from the East, settled in Palestine already about 2600 B. C. To some extent the spread of this index also coincides with what we know concerning the geographical distribution of the *Amorites*.

BÖHL<sup>1)</sup> stated that they lived in the valley between the Lebanon and Antilebanon — the present Beká — further in Palestine (Szichem) and on the desert border from Transjordan to Damascus and further up to North Syria. Similar indications are found with ED. MEYER<sup>2)</sup>. ALBRIGHT<sup>3)</sup> states that the *Amorites* — in contradistinction to the Kanaanites (the Phoenicians of the coast) — lived on the eastern slopes of the Lebanon and on the desert border from where they invaded Palestine. Finally the occurrence of this index in Mesopotamia, if Amoritic, might be explained by the Amorite invasion of that country (2200—1900 B. C.) before and under Hammurabi, where later they were beaten by the Hittites.

Concerning the racial characteristics of the *Amorites* very little is known. The supposition, based on Amorite pictures in Egyptian monuments by SAYCE<sup>4)</sup>, FLINDERS PETRIE<sup>5)</sup> and CLAY<sup>6)</sup> that they were fairhaired, blue eyed proto Nordic dolichocephalics is contested by AUERBACH<sup>7)</sup>, BÖHL, BAUER, MEYER and RUPPIN<sup>8)</sup>, who consider them as Semites racially as well as linguistically, closely related to the Hebrew tribes. RUPPIN even considers Amorite mixture as a strong factor in the ascendancy of the Hebrews, after their Palestinian invasion, by marriages with Amorite women.

<sup>1)</sup> BÖHL. Kanaanäer und Hebräer. Beitr. z. Wiss. vom alten Testament 1911; *The same*: Kanaan, Intreerede Groningen 1913; *The same*: Bijbelsch Kerkelijk Woordenboek. Het Oude Testament, p. 20.

<sup>2)</sup> ED. MEYER. Geschichte des Alterthums. Bnd 1, 2te Hälfte, 5te Auflage, Stuttgart u. Berlin 1926, p. 614 a. f.

<sup>3)</sup> Journal of the Palestine Oriental Society Jerusalem, Vol. VIII, 1928, p. 255.

<sup>4)</sup> SAYCE. The white race of ancient Palestine. The Expositor, Vol. 8, 1888 and The Races of the Old Testament, 1925.

<sup>5)</sup> FLINDERS PETRIE. Nature 1888.

<sup>6)</sup> CLAY. The empire of the Amorites 1919, quoted from GÜNTHER, Rassenkunde des jüdischen Volkes. Lehmann, München, 1931, p. 54.

<sup>7)</sup> E. AUERBACH. Die Jüdische Rassenfrage. Arch. f. Rassen- u. Gesellsch. Biologie. Jahrg. IV, Heft 3, 1907, p. 332.

<sup>8)</sup> RUPPIN. Soziologie der Juden. Jüd. Verlag Berlin, p. 23.

But the Amorites may have belonged to an Adnan Arab stem, as may find some support in the fact that they were specially numerous in South-Palestine and Southern Transjordan (AUERBACH) where the Adnan index still prevails and probably prevailed<sup>1)</sup>. Besides SAYCE and FLINDERS PETRIE believe the Amorites were exquisite dolichocephalic.

That the 81 index group is racially different from the Adnan index group (77), even appears from the desert border and Palestinian Arab curves, in both of which Adnan tops occur in addition to the 81 top — thus indicating the difference between the main (81) race and the Phoenico-Palmyrene group, living amongst them.

A third, entirely different possibility may not be left out of consideration here, i.e. that the index 81 results from a mixture of Hittite and Phoenico-Palmyrene blood. The fact that this intermediate index is found especially in those places where exquisite brachycephalics are bordering on mesocephalics makes this quite probable on first sight. For this point the consequences of such a mixture have to be considered, especially the question whether such marriages — if they happened frequently — would give an offspring with an intermediate index or if only the range of variations would increase with them.

Researches in this direction are made by BOAS<sup>2)</sup> on LIVI's<sup>3)</sup> figures concerning the population of Italy.

In Italy two types of headform are represented both with moderate variabilities, but with different averages, that of Southern Italy with a low average index, that of Northern Italy with a high average index. BOAS then says:

"The variabilities of these two types bring it about that in central Italy we find very low values which belong to the Southern type and very high values which belong to the Northern type, so that the whole area has a wide range of variation expressed in a high variability. If a uniform type should develop through mixture we should expect a lesser range of variation." This agrees with VON LUSCHANS experience in Turkey<sup>4)</sup> that there is a tendency in racial mixtures to revert to the ancestral types and not form an intermediate type. It also agrees with my personal experience with the offspring of mixed Sephardim-Aschkenasin marriages.

The range of variation in my desert border population being relatively small confirms my belief that we may consider this group as a group of its own, not as the result of a mixture. The distinctness with which its top returns among other indices in the Lebanon and in Irak is also in favor of this conclusion. Besides if such marriages had been quite

<sup>1)</sup> BÖHL is even inclined to consider the Hyksos that invaded Egypt (1800—1600 B. C.) as Amorites. (Bijbelsch Kerkelijk Woordenboek.)

<sup>2)</sup> F. and H. BOAS. The headforms of the Italians as influenced by heredity and environment. *American Anthropologist*, Vol. 15, 1913, p. 165.

<sup>3)</sup> LIVI. *Anthropometria militare*, 1896 and The same: *Arch. per l'Anthrop. l'Etnologia*, Vol. 16, p. 254. Quoted from BOAS whose opinion seems to be confirmed by GINI's paper: *Variabilità e Mutabilità*, Bologna, 1912.

<sup>4)</sup> V. LUSCHANS. Die Tachtadschy und andere Ueberreste der alten Bevölkerung Lykiens. *Arch. f. Anthrop.* Vol. 19, 1891, p. 311.

frequent the Hittite index — on account of its dominating character would prevail — as it does in Irak.

As far as concerns the reasons for the anthropological differences amongst the present Jews — the Sephardim and Aschkenasim especially — we must consider this in the same light, and first of all be aware of the fact that only 8 % of the present Jews are Sephardim while the remaining 92 % are Aschkenasim (RUPPIN, l.c. p. 59).

WEISSENBERG and PITTARD <sup>1)</sup> with him (l.c. p. 345) believe that the Sephardim may have a closer relation with the original Hebrews than the Aschkenasim. But the typical index of the male Sephardim is about 77—78 (c.f. also WAGENSEIL <sup>2)</sup>) while the original Hebrew index, according to the Megiddo skulls and to the overlapping of the Sephardim and Aschkenasim curves at 80—82 was higher. So I am inclined to accept SZPIDBAUM's <sup>3)</sup> standpoint that the Sephardim are strongly mixed with Arabic Semites. This opinion is supported by the fact that the Beduin and Sephardim curves coincide in their typical top (fig. 6).

Besides — as was already stated by SZPIDBAUM the bloodtype of the Sephardim is very near to the Arabic bloodtype (L. and H. HIRSZFELD <sup>4)</sup>, and HALBER and MYDLARSKI <sup>5)</sup>).

In this respect I also want to call the attention to the extensive blood-group work of W. L. PARR <sup>6)</sup> (also quoted by SNIJDER <sup>7)</sup> ).

Just as with the more than 1800 Maronites, i.e. Lebanese, tested by PARR, the racial bloodindex (2.56) is nearly the same as with the Armenians (2.31) and Khaldeans (2.19) thus confirming their Armenoid relationship, so the fact that with his Moslem Arabs — probably nearer related to the Syrian Adnan Arabs the racial bloodindex (1.59) <sup>8)</sup> is nearly the same as with his Sephardim (1.33; 1.17, YUNOWITSCZ) is strongly in favor of this thesis.

As far as concerns the very high brachycephalic index of a great many

<sup>1)</sup> PITTARD. Race and History.

<sup>2)</sup> WAGENSEIL. Beiträge zur physischen Anthropologie der spaniolischen Juden und zur jüdischen Rassenfrage. Zeitschr. f. Morphologie u. Anthropologie, Bnd 13, 1918.

<sup>3)</sup> L.c. supra and SZPIDBAUM. Altes und Neues über die Anthropologie der Juden. Ose Rundschau, 1ste Jahrg. No. 3, Sept. 1926, p. 4, and Ibidem 2te Jahrg. No. 2. Febr. 1927, p. 7.

<sup>4)</sup> L. and H. HIRSZFELD 1919, quoted from SNIJDER (see below).

<sup>5)</sup> HALBER and MYDLARSKI. Compt. rend. Soc. de Biol. Vol. 89, 1923. Zeitsch. f. immun. Forsch.; Vol. 43, 1925.

<sup>6)</sup> W. L. PARR. Studies in isohemagglutination. Journal of Immunology, Vol. 16, 1929, and Die Blutgruppenverteilung in der Bevölkerung des nahen Osten und Nord-Afrika. Ukrainisches Zentralblatt für Gruppen Forschung Bnd. IV, 1930.

<sup>7)</sup> SNIJDER. Bloodgrouping in relation to clinical and legal medicine; Williams and Wilkins, Baltimore, 1829.

<sup>8)</sup> With the Egyptian Arabs PARR found a lower bloodindex (1.30).

Aschkenasim VON LUSCHAN<sup>1)</sup> was the first to explain this by admixture with Hittites, whose prevailing indices, considering the Armenians as their

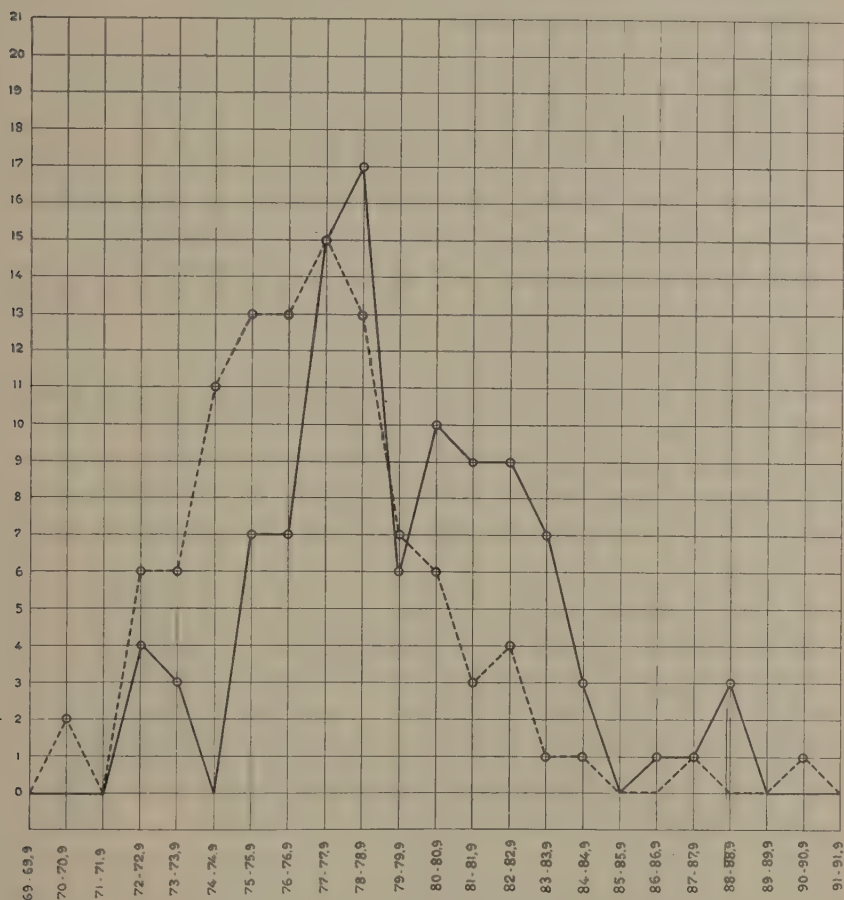


Fig. 6. Dotted line = Beduins; thin continuous line = Sephardim.

nearest living relatives, was about 83 and 86 (see my first contribution). Also the Jewish nose, more typical with the Aschkenasim than with the Sephardim might be explained by this admixture (cf. FISHBERG l.c. infra, p. 51). While marriages with Hittite women were no exception with the Jews, specially in preexilic times (cf. AUERBACH<sup>2)</sup> and FISHBERG<sup>3)</sup>), the

1) VON LUSCHAN, Die Anthropol. Stellung der Juden. Korr. bl. der Deutschen Gesellsch. f. Anthropol. 1892. See also the same: Jews and Hittites, Science, 1894 and the same: Offener Brief an Herrn Dr. ELIAS AUERBACH, Arch. f. Rassen u. Gesellsch. Biol. Jahrg. 1907, p. 362.

2) E. AUERBACH. Die jüdische Rassenfrage, ibidem, p. 332.

3) FISHBERG. Die Rassenmerkmale der Juden, München, Ernst Reinhardt, 1913.



Armenoid influence is also probable by the fact that the Aschkenasim are spread especially in Northern direction (the Sephardim South, West and East), and the Northern races amongst whom they lived were mostly brachycephalics. Besides we know that brachycephaly is dominant in heredity.

An interesting example of this is the fact found by CHANTRE that the Jews and Kurds living near Lake Urmiah in Old Armenia have the same index as the Armenians of that district (86.1).

Still E. AUERBACH's warning that the role of the Hittites in such admixtures should not be exaggerated is right, not only for AUERBACH's historical arguments (see specially p. 346 of his paper), and for the fact that hypsicephaly is frequent with Armenoid races and not with Jews, but also for the fact that hyperbrachycephaly is much more general with Armenoid races than with the Aschkenasim. Though higher indices do occur with them their average is only about 82.5.

I agree with AUERBACH that the original Hebrew-index itself was probably subbrachycephalic, and that in addition to the Armenoids other brachycephalic races may have enlarged this index (WEISSENBERG l.c.) the more so as according to FISHBERG (l.c. p. 31), the Aschkenasim index frequently shows some adaptation to the index of the non-Jewish peoples amongst whom they live. That this adaptation is specially seen in a strongly brachycephalic environment may be due to the hereditary dominance of brachycephaly.

Also the work of BOAS<sup>1)</sup> is to be mentioned here. BOAS found that the offspring born from Jewish parents just immigrated into America have an average index (81.4) lower than the average parental index (83). He observed a similar process but not nearly as striking with the Armenians<sup>2)</sup>.

Though these results, according to BOAS himself do not take away the evidence of a great stability of types, they should be seriously considered (cf. also FEIST<sup>3)</sup>).

Taking the figures found by BOAS as facts, it is remarkable that, whereas the Jewish index decreases, the Sicilian index increases<sup>4)</sup> and that both approach the figure 81.5.

Considering the fact that 81.5 is a very frequent perinatal index — even with people whose adults are mesocephalics, one might ask if BOLKS<sup>5)</sup> fetalisation theory may give an explanation here.

1) BOAS. Changes in bodily form of descendants of immigrants. Report of the Immigration Commission, Washington, 1911 and American Anthropologist, Vol. 14, 1912, p. 530.

2) BOAS. Bemerkungen über die Anthropometrie der Armenier, Zeitschr. f. Ethnologie. Bnd. 56, p. 74.

3) FEIST. Stammeskunde der Juden. p. 174, 183.

4) See the above mentioned report of the Immigration Commission and BOAS, The Headform of the Italians as influenced by heredity and environment. Am. Anthropologist. Vol. 15, 1913, p. 163.

5) BOLK. On the Problem of Anthropogenesis. These Proceedings, Vol. 29, 1926, and BOLK. On the origin of human races. These Proceedings, Vol. 30, 1927. See also BOLK Das Problem der Menschwerdung, Fischer Jena, 1926.



In connection herewith the work of HIRSCH<sup>1)</sup> should be mentioned. This author confirming BOAS' statements in his researches on the cephalic index of American born children of three foreign groups (South-Italians, Russian Jews and Swedes) is inclined to explain the cephalic changes with the Jews (where they are more remarkable than with other races) to mental influences causing changes in the endocrine system.

Nevertheless the results of comparative anthropology in the Near-East still give sufficient evidence for the hereditary value of the cephalic index in migrations that do not involve such sudden and great environmental changes as transatlantic migrations to America do. At least my own researches, covering more than 2500 individuals, connected with the work of PARR and others on bloodtypes confirm rather than shake the belief in this hereditary value, provided we take in consideration the hereditary predominance of brachycephaly (FRETs), that certainly acts a part in the prevailing occurrence of an increased degree of brachycephaly with the Aschkenasim.

I finish with a list of the head indices of the various "Hittite" races and the Arabic and Hebrew Semites comparing them with the racial blood index  $\frac{A+AB}{B+AB}$  of these groups as found by PARR, HALBER and MYDLARSKI, the HIRSZFELD's, SCHIFF and ZIEGLER<sup>2)</sup>.

Group	l. w. i.	Blood ind.	Group	l. w. i.	Blood ind.
Egypt. Arabs	75.89	1.30	Germ. Aschk. (Baden)	83.50 <sup>3)</sup>	2.91
Mosl. Adnan (?) Arabs	76.85	1.59	Armenians	86.11	2.31
Sephardim	79.01	1.33	Lebanese Maronites	85.99	2.56
Samaritans	77.23	2.35	Khaldeans	86.01	2.19
Polish Aschk.	81.89 <sup>3)</sup>	2.00			

From this it appears that on the whole there is a great agreement in the results: the bloodindex being 2 or more with the brachycephalic races and less than 2 in the mesocephalics of my list. An exception are the Samaritans, who however in addition to their Phoenician stock certainly contain a Jewish contingent (Samaria being the old capital of the Northern Kingdom). Besides the Samaritans are a strongly inbreeding group and in such groups the *A* as well as the *B*, once present, may dominate (VAN HERWERDEN), an exemple of *B* domination being given by the highly brachycephalic Druses (l.w. index 87.26, bloodindex 1.59 PARR). —

<sup>1)</sup> HIRSCH. Journal of physical Anthropol. Vol. X, 1927, p. 79.

<sup>2)</sup> Quoted from SNIJDER, (l.c.).

<sup>3)</sup> Quoted from FISHBERG (l.c.).

From this it appears one has to be careful in assuming a *constant* correlation between the blood- and head index, the more so, since KLEIN<sup>1)</sup> in Westphalia (Herne) found a higher *B* and consequently a smaller blood-index with the brachycephalics compared to his dolichocephalics, and in Finnland (STRENG)<sup>1)</sup> and Holland (VAN HERWERDEN)<sup>1)</sup> no correlation whatever could be detected.

This does not, however, minimize the fact that the bloodindices of the Near East groups largely support the anthropological relationships established on account of the headindex and vice versa.

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1) See VAN HERWERDEN, Investigation of bloodgroups in Holland, Proceed, Kon. Akad. v. Wetensch. Amsterdam . Vol. **33**, 1930, p. 659.

**Anatomy.** — *Die Terminalbeuge des Vorderhirns bei den Chordaten und die protischen Nerven der Kranioten bei Amphioxus.* Von J. W. VAN WIJHE. (Aus dem Anatomisch-Embryologischen Laboratorium in Groningen).

(Communicated at the meeting of January 31, 1931).

### *Erste Mitteilung.*

Im vergangenen Jahrhundert herrschte in der vergleichenden Anatomie die „Wirbeltheorie des Schädels“, nämlich die Meinung, dass der Schädel der Wirbeltiere aus knöchernen oder knorpeligen Wirbeln aufgebaut sei. Die Segmentierung der Wirbelsäule sollte auch dem Bau des Schädels zu Grunde liegen.

Jetzt wird es wohl nur wenige mehr geben, welche dieser Meinung sind, denn nicht nur ist kein einziges Tier bekannt geworden bei welchem der Schädel noch aus Wirbeln besteht<sup>1)</sup>, sondern auch in der Entwicklungsgeschichte hat man dieselben bei keinem Embryo nachweisen können.

Der Gedanke aber, welcher der Wirbeltheorie zu Grunde liegt, dass nämlich der Kopf ursprünglich, ähnlich wie der Rumpf, segmentiert gewesen sein muss, hat sich als richtig herausgestellt.

Man muss dabei aber nicht das phylogenetisch jüngste, das Skelettsystem, sondern die phylogenetisch älteren Muskel- und Nervensysteme ins Auge fassen<sup>2)</sup>.

Nach der grundlegenden Arbeit von BALFOUR (1878) trat im letzten Viertel des vorigen Jahrhunderts nicht mehr die Anatomie, sondern die Entwicklung des Kopfes in den Vordergrund des Interesses einer grossen Menge von Forschern. Einer von diesen meinte die Zahl der Kopfsegmente auf drei beschränken zu können, die anderen aber glaubten dieselbe auf das vielfache, bis ins Unbestimmte vergrössern zu müssen.

Es war dies eine stürmische Periode, die man auch mit einem Ausdruck

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1) Die selbständig auftretenden knorpeligen Wirbelelemente, die bei einigen Fischen mit dem hinteren Teile des Schädels verschmelzen, können nicht als integrierende Bestandteile des Schädels der Wirbeltiere aufgefasst werden.

2) BALFOUR hat den ersten wichtigen Anstoss zur Entwicklungsgeschichte dieser Systeme bei Selachiern gegeben. Er fand die Anlage der dorsalen Hirn- und Spinalnerven in der Nervenleiste und entdeckte die Kopfhöhlen aus deren Wand er die Entstehung von vielen Kopfmuskeln beobachtete (1878, p. 208).

Vor ihm hatte GEGENBAUR die Anatomie der Kopfnerven (und Kiemenbogen) in seine Betrachtungen über die Segmentierung des Schädels aufgenommen.

von GÖTTE aus den Anfängen der Wirbeltheorie als *tumultuarisch* bezeichnen kann. In dieser Periode war man geneigt den *Amphioxus* als Unkraut aus dem Garten der Wirbeltiere hinauszuerwerfen. Heutzutage aber ist er wieder zu Ehren gekommen. ARIËNS KAPPERS hat ihm denn auch den gebührenden Platz eingeräumt in zwei schönen Arbeiten, nämlich in seinem grossen Handbuch (1920 und '21) und in seinem bündigen Lehrbuch (1929).

In unserem Jahrhundert hat sich der Sturm allmählich gelegt, aber eine allgemeine Vereinbarung über die Zahl der Kopfsegmente und die Analyse der Kopfnerven ist noch lange nicht erreicht. Doch glaube ich, dass dies noch vor dem Ende des Jahrhunderts der Fall sein kann. Die beiden oben erwähnten Bedingungen nämlich, welche der Wirbeltheorie abgingen, werden bei der „Segmenttheorie“ erfüllt, denn: 1<sup>0</sup>. es existiert nicht nur eine Tiergruppe, die Homomerier (Akranier) bei welchen Kopf und Rumpf gleichmässig segmentiert sind, sondern 2<sup>0</sup>. auch die Embryonen höherer Tiere zeigen die Spuren dieser Segmentierung mehr oder weniger deutlich.

Die Gruppe der Homomerier zählt, meines Wissens, bis jetzt nur zwei Genera: *Amphioxus* und *Asymmetron*, da *Amphioxides* (GOLDSCHMIDT) als Larve von *Asymmetron* zu betrachten ist.

Bei den höheren Tieren wird die Segmentierung des Kopfes undeutlich, hauptsächlich durch zwei verschiedene Kraftkomplexe, welche in entgegengesetztem Sinne die Myotome beeinflussen.

Der eine Komplex geht von der Ohrblase aus, welche als Gleichgewichtsorgan auftritt. Dieselbe hat Myotome vernichtet, teilweise nur zum Degenerieren gebracht, weil das Gleichgewichtsorgan im Körper nicht beweglich sein darf, sondern fest stehen muss (anfangs durch eine Art Bindegewebe „Vorknorpel“, später mittels der knorpeligen Parachordalia an die Chorda dorsalis befestigt) damit dasselbe die Stellung des ganzen Körpers reflektorisch regeln könne<sup>1)</sup>.

Der andere Kraftkomplex geht vom Augapfel aus, der nicht im Körper feststehend, sondern im Gegenteil beweglich sein muss. Derselbe hat durch seine kugliche Form<sup>2)</sup> Reste von so vielen prootischen Myotomen vom Untergange gerettet, als nötig waren den Augapfel in sämtliche Richtungen drehen zu können.

Die Homomerier haben weder Augapfel noch Ohrblase und so ist es begreiflich, dass die Reihe ihrer Myotome nicht in der Kopfregion unterbrochen wird, sondern dass dieselbe ähnlich wie die Rumpfregion durch Muskelsegmente und periphere Nerven abgeteilt ist.

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<sup>1)</sup> Die Ohrblase ist zwar der hauptsächlichste, aber nicht der einzige Vernichter von Myotomen in der Kopfregion. So geht z. B. am Auge der Selachier der embryonale Muskel *E* (sieh eine spätere Mitteilung) zu Grunde, während bei *Amphioxus* der larvale praeoralmuskel im Laufe der Metamorphose verschwindet.

<sup>2)</sup> Bei den Myxinoiden ist die Form der primitiven Augenblase nicht kuglich, sondern länglich. Deshalb sind nicht sämtliche Bewegungen möglich und so sind auch die prootischen Myotome, sogar in der Ontogenese, verschwunden.

Freilich geht auch bei ihnen ein Myotom, das erste der Reihe in der Kopfgregion der Larve, während der Metamorphose verloren. Der Präoralmuskel desselben wurde von GOLDSCHMIDT (1905) bei Amphioxides entdeckt. Ich fand denselben auch bei älteren Amphioxuslarven. Er liegt mit Ursprung und Insertion links von der Medianebene im rechten Entodermsäckchen HATSCHES 1).

Ich kann nicht bezweifeln, dass dieser Muskel der Oculomotoriusmuskulatur der Kranioten entspricht, weil er wie diese Muskulatur aus Zellen einer Abschnürung des präoralen, vordern Entodermes entsteht.

Der kleine Präoralmuskel muss durch einen sehr feinen Oculomotorius versorgt sein, der sich bis jetzt der Beobachtung entzogen hat und nur bei der Larve, nicht mehr nach der Metamorphose, erwartet werden kann.

Es drängt sich jetzt die allgemeine Frage auf: Welche Muskel- und periphere Nervensegmente, die bei Amphioxus noch getrennt sind, beteiligen sich am Kopfe der Kranioten?

Wir werden diese Frage in einer folgenden Mitteilung in Betreff des Trigemini und der Ventralnerven seiner Segmente zu beantworten versuchen, müssen aber erst den N. terminalis und das Geruchsorgan besprechen.

#### *Der N. terminalis und die Terminalbeuge des Vorderhirns.*

Es darf heute wohl für festgestellt gehalten werden, dass der N. terminalis als ein typischer Vorderhirnnerv der Chordaten betrachtet werden muss. Bei den wenigen Formen wo er zu fehlen scheint (Petromyzon, einigen Teleostiern 2)) muss angenommen werden, dass er abortiert ist.

Bei Amphioxus habe ich ihn früher (1894) N. apicis genannt und mit dem damals von PINKUS bei Protopterus entdeckten neuen Nerven homologisiert.

1) Der Präoralmuskel entspringt von einem Punkte, links am Unterrand der Chorda. Von dort wendet er sich, fächerförmig ausgebreitet, kaudalwärts und inseriert in die Haut, hart neben der Unterlippe des Präoralorgans.

Die Muskelplatten sehen mit der einen Seitenkante frei in das Myocöl aus; die andere Seitenkante bleibt der Haut angeheftet und macht sich nicht von derselben frei. Kontrahiert sich der Muskel, so zieht er die Unterlippe des Präoralorgans rostralwärts und muss er dasselbe öffnen (nicht schliessen, wie GOLDSCHMIDT meint). Den Schliessmuskel bilden die vorderen Fasern des Mandibularmuskels, welche vor dem Munde (Tremostoma) an die Basis der Mandibularpapille inserieren.

Die linksseitige Lage des Präoralmuskels im „rechten“ Entodermsäckchen spricht für die Auffassung, nach welcher das Säckchen morphologisch eine mediane Bildung ist. Nach dieser Auffassung ist das Antimer des Präoralmuskels auf der rechten Körperseite abortiert.

2) Bei manchen Teleostiern scheint man Zweige des N. olfactorius für solche des N. terminalis gehalten zu haben. Vgl. meine Übersicht über den Nerv bei verschiedenen Wirbeltiergruppen (1918).



Er ist bei *Amphioxus* der vorderste der Hautnerven und wurde von GOODSIR (1841) entdeckt. Er wurde später von anderen manchmal übersehen, ist aber konstant und paarig vorhanden.

Der Nerv versorgt die Haut der Schnauzenspitze am vorderen Chordaende. Sein Endigungsgebiet liegt sowohl über als unter der Chorda und seitlich von derselben, so dass eine dorsale und ventrale Verzweigung nur künstlich getrennt werden können, indem man sich eine frontale Ebene hart über der Chorda gelegt denkt.

Ich habe (1901, Taf. XI, Fig. 34) den Nerv der rechten Körperseite mit sämtlichen Zweigen, soweit dieselben sichtbar waren an einem Präparat nach Wegpinselung der Epidermis, abgebildet. Vom folgenden Nerven (der dem N. nasociliaris entspricht) sind nur die groben Zweige und einige wenige feinere in der Figur angegeben. Die Ganglienzellen an beiden Nerven sind bei der Pinselung verloren gegangen.

Am 2. Nerven (Nasociliaris) der hart hinter der Vorderhirnblase hervortritt, kann man schon leicht einen Ram. dorsalis und Ram. ventralis unterscheiden, da zwischen diesen beiden Zweigen das Hautfeld des N. terminalis eingeschoben ist. Die Hauptrichtung beider Zweige zieht aber weder dorsal- noch ventralwärts, sondern vorwärts.

Der 3. (nicht abgebildete) Hautnerv ist gleichfalls rein sensibel. Seine dorsale und ventrale Verzweigung liegen hinter der Schnauze. Nur ein ganz feiner Zweig beteiligt sich noch an der Versorgung des hinteren Endes der ventralen Schnauzenflosse. Dieser Zweig ist noch stark vorwärts gerichtet. Aber der Ram. dorsalis steigt schon, wie bei folgenden Nerven, fast senkrecht empor.

Diese Verlaufsrichtungen werden uns aber erst beim N. trigeminus interessieren; wir wollen zum N. terminalis zurückkehren.

Wegen der peripheren Endigung desselben in der Haut der Schnauzenspitze (bei den Kranioten scheint er auf das Nasenepithel beschränkt zu sein) gehört der Nerv unzweifelhaft zu der Gruppe der Dorsalnerven (Septalnerven).

Damit scheint aber seine zentrale Fortsetzung in flagrantem Widerspruch, denn dieselbe liegt am „Boden“ der Vorderhirnblase, wo sie in der Richtung zum Infundibularorgan zu verfolgen ist<sup>1)</sup>.

Der Widerspruch ist aber nur scheinbar, wie das Verhalten der Neuralrinne bei Kraniotenembryonen zeigt.

Bei Torpedoembryonen nämlich bildet die Neuralrinne, nachdem sie sich schon grossenteils vom Hautektoderm abgeschnürt hat, noch am „Boden“ der Vorderhirnblase einen medianen, offenen Schlitz (Neuroporus) zwischen den Augenblasen. Mit anderen Worten: bei diesem Tiere ist die Verschlusslinie des Neuralrohres am Vorderhirn ventralwärts umgebogen wie die umgebogene Handhabe eines Spazierstocks oder eines Regenschirms.

<sup>1)</sup> Hierauf hat KAPPERS (1821, p. 962) in seinem Handbuche aufmerksam gemacht.

Man kann diese bekannte Krümmung des Vorderhirndaches die Terminalbeuge<sup>1)</sup> nennen. Dieselbe endet an der Vorderwand des Infundibulums und muss für sämtliche Chordaten angenommen werden, wie wir sofort sehen werden.

Ich habe einen Querschnitt durch den Neuroporus zwischen den Augenblasen bei einem Torpedoembryo aus BALFOURS Stadium G abgebildet (1882, Taf. 4, Fig. 27). Die Gebrüder ZIEGLER zeichnen einen solchen aus dem nächst jüngeren Stadium F (1891, Taf. 4, Fig. 21). Dieser und die übrigen von ihnen beschriebenen Embryonen sind auch in den berühmten Wachsmodellen dess Herrn F. ZIEGLER reproduziert.<sup>2)</sup>

Auf Grund der Verhältnisse bei Haifischembryonen muss man annehmen, dass sich der schlitzförmige Neuroporus bei Torpedo hauptsächlich verkleinert, indem der dammartig verdickte Hinterrand allmählich *topographisch* vorwärts rückt. So bildet sich der „Boden“ der Vorderhirnblase, welcher sich gleichzeitig vom Hautektoderm abschnürt. Infolge dessen wird der Zusammenhang von Haut und Hirn zuletzt in der Nasenregion gefunden.

Wenn nun bei Rochen der Vorderhirnboden dorsal liegt, so muss dies auch bei den Haifischen der Fall sein, obgleich man, meines Wissens, bei denselben nie den Neuroporus zwischen den Augenblasen, d. h. bis an den Vorderrand der Infundibulums, offen gesehen hat. Man muss hier am scheinbar ventralen Boden des Vorderhirns einen vorzeitigen Verschluss annehmen, der von der Augenregion topographisch vorwärts (morphologisch aber rückwärts) zur Nasenregion zieht.

1) HATSCHKE (1909, p. 519) in seinen Untersuchungen über die Entwicklung von Petromyzon, hat diese Krümmung als „Ueberwölbung des vordersten Teiles des Medullardaches“ bezeichnet.

2) Ich möchte hier noch auf eine beachtenswerte Eigentümlichkeit des Verschlusses des Neuralrohres aufmerksam machen, was die Verfasser im Texte unterlassen haben. Nämlich dass die Epidermis sich im vorderen Köperteil (Mittel- und Hinterhirn) schon über der Neuralrinne verlötet, bevor sich die Neuralplatte zum Rohre geschlossen hat (1891, Fig. 21 II bis 21 IV). Dieser vordere Verschluss geschieht ähnlich wie beim Amphioxus.

Am Rückenmark aber (Fig. 21 V) finden wir denselben Typus wie bei anderen Kriechtieren, indem der Verschluss des Neuralrohres und die Verlötung der Epidermis gleichzeitig stattfinden.

Die ZIEGLERSchen Abbildungen zeigen noch eine andere, sehr bemerkenswerte Uebereinstimmung der Selachier- mit Amphioxus-Embryonen, nämlich den grossen Umfang des Blastocöls, in welches das Mesoderm in diesen frühen Stadien der Segmentierung hineinwächst.

Auch bei Amphioxus tritt in diesen frühen Stadien der Segmentierung das Blastocöl (welches bei der Gastrula zeitweilig verschwindet) wieder auf, und erreicht einen beträchtlichen Umfang, wie man bei CERFONTAINE (1906, Taf. 22, Fig. 1 ; 3 bis 6 ; 7 bis 9 ; 10 bis 18) sehen kann. Zwar scheint er die Höhle für ein Artifact zu halten (l. c. p. 379), wie auch spätere Autoren bei etwas älteren Stadien tun. Ich konnte das Blastocöl aber nicht nur auf Schnitten und an Präparaten in toto, sondern auch am lebenden Objekte wahrnehmen. Noch vor dem Durchbruch der Mundöffnung ist dasselbe wieder grossenteils verödet.

Die Verschlusslinie ist an der Epidermis gekennzeichnet durch eine mediane Verdickung, eine Art Rhaphe, (vgl. meine Abbildung, 1882, Fig. 28, Stad. G) die später sich teilend, beiderseits zur Nasenregion (Fig. 29, *ep'*, Stad. I) emporsteigt<sup>1)</sup>).

Wie auch von anderen schon gelegentlich bemerkt und von PETER (1901a) eingehend beschrieben wurde, kommen hier an letzter Stelle des Zusammenhangs von Hirn und Epidermis zwei verschiedene Verschlussarten des Neuralrohres zusammen, die man als *Seitennaht* und *Endnaht* bezeichnen kann. Man kann dieselben auch bei dem Verschluss von Öffnungen an anderen Organen nachweisen.

Bei der *Seitennaht* legen sich die Seitenränder einer schlitzförmigen Öffnung vor der Verlötung aneinander. Bei der *Endnaht* geschieht dies nicht, sondern das eine (wohl meistens abgerundete und verdickte) Ende wächst auf das andere Ende der Öffnung hin<sup>2)</sup>).

Auch bei Vogel- und Eidechsenembryonen erstreckt sich der spaltförmige Neuroporus bis zwischen den Augenblasen. Wenn dies nun bei Säugetieren und Amphibien nicht der Fall ist, so muss man auch hier, wie bei den Haifischen nach meiner Ansicht, einen vorzeitigen Verschluss der Endnaht in der Augengegend annehmen.

Bei Ascidien biegt' sich der Neuroporus ventralwärts um, bis in das Stomodaeum, so dass auch bei dieser Gruppe eine Art Terminalbeuge der Hirnblase vorkommt.

Bei Amphioxus dagegen bleibt der Neuroporus (resp. die Riechgrube) in dorsaler Lage. Der Ursprung des (dorsalen) N. terminalis am sog. „Hirnboden“ weist aber darauf hin, dass man auch hier an diesem sog. Boden einen vorzeitigen Verschluss der Endnaht annehmen muss.

Bei Petromyzonembryonen fand HATSCHEK (1909, 1929) nach sorg-

1) Ich habe damals diese Stelle *ep'* unrichtig für die Region der Epiphyse gehalten aber den Fehler nachträglich (1884) verbessert (vgl. auch die Amm. 5, p. 52 der 2. Ausgabe, 1915) indem ich fand, dass es sich hier um die Nasenregion handelt, wie auch HOFFMANN (1896) und LOCY (1905) gefunden haben.

2) Beide Nähte können in einander übergehen: Der Verschluss der Rückenmarksrinne bei Amphibien- und Ammietenembryonen, geschieht in eine typische Seitennaht. Aber die Verlötung der Epidermis über der Neuralrinne bei Amphioxus und Ascidien ist eine Endnaht, indem das Hinterende derselben (ohne das Aneinanderlegen der Seitenränder) allmählich vorwärts rückt. Bei Ascidien hat es dadurch den Anschein als rücke der Blastoporus vorwärts.

Auch bei Amphioxus konnte man dies glauben, bis CERFONTAINE (1906, p. 355, 356) SAMASSA bestätigend, fand, dass die Verlötung der Epidermis eine kurze Strecke vor dem Blastoporus anfängt.

Eine Endnaht kommt an anderen Organen als das Zentralnervensystem vielfach vor. So geschieht der Verschluss des langen schlitzförmigen Mundes der Amphioxuslarve, indem das hintere Ende des Schlitzes vorwärts rückt. Ein anderes Beispiel ist die teilweise Abschnürung der kolbenförmigen Drüse vom Darm nach GOODRICH (1930, Schema, p. 163).

Bei den plazentalen Säugetieren geschieht die Teilung der Kloake in Rektum und Sinus urogenitalis durch Endnaht. Auch ist der Verschluss der Penisrinne, bis auf einen kleinen Spalt, wohl als Endnaht aufzufassen.

fältiger Untersuchung dass an der noch soliden Vorderhirnanlage die dorsale Schlussnaht sich ventralwärts fast bis zur „Hypophysenecke“ umbiegt. Schon LUBOSCH (1902, Fig. 1, 2) fand, dass der solide Neuroporus fast bis zur Hypophysenanlage hinunterreicht.

Nach der obigen Auffassung existiert die Terminalbeuge des Vorderhirns bei sämtlichen Chordaten, von den Tunikaten und Amphioxus ab bis zum Menschen.

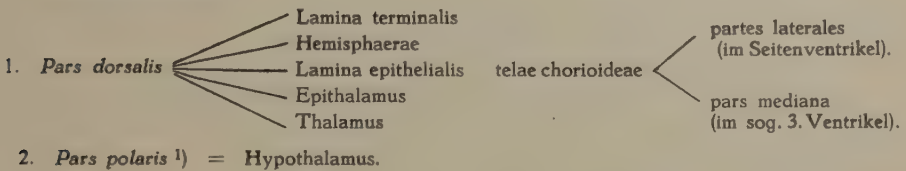
Bei Amphioxus ist sie die einzige Hirnbeuge, da hier selbst die Mittelhirnkrümmung fehlt, welche sämtlichen Kranioten zukommt.

Ich glaube, mancher Leser wird dieselbe oder eine ähnliche Auffassung haben und finden, dass ich mich zu lange dabei aufhielt. Ich habe dies aber für solche Leser getan, die von den Säugetieren oder Amphibien ausgehen und glauben, hier primitive Verhältnisse beim Verschluss am vorderen Ende der Neuralrinne anzutreffen.

Mit HIS war ich immer einverstanden, dass das morphologische Ende der Neuralrinne am Infundibulum liegt. Dann tritt der Optikus aber nicht aus dem *Diencephalon*, sondern wie der Terminalis und der Olfactorius aus dem *Telencephalon*.

Die gebräuchliche Teilung des Prosencephalons in Telencephalon und Diencephalon ist doch eine sehr künstliche. Es scheint besser dieselbe ganz fallen zu lassen und das Vorderhirn folgender Weise einzuteilen:

### Prosencephalon:



Eine eigentliche pars ventralis, im Sinne einer solchen wie am Mittelhirn und Hinterhirn, in welcher die Kerne der motorischen Nerven liegen, kommt am Vorderhirn nicht vor. Der Sulcus limitans setzt sich nicht in das Prosencephalon fort, sondern endet am Vorderende des Mittelhirns.

Nennt man die Hirnventrikel (Pro-, Meso-, Meta-) Neurocöle, so zerfällt das PRONEUROCÖL in:

- a. *Partes laterales* (Ventriculi laterales).
- b. *Pars mediana* (sog. Ventriculus tertius).

1) Am Hinterrand des Infundibulums liegt der vordere Pol der Körperachse, die durch die Mitte der Chorda zieht (nur bei den Homomeriern wächst dieser Pol sekundär rostralwärts in die Schnauze hinein). Auch liegt hier der vordere Pol der Mesodermsegmentreihe mit der medianen Verbindung des linken und rechten 1. Segmentes.

Am Vorderrand des Infundibulums liegt der morphologisch vordere Pol der Rhaphe des Neuralrohrs.



### Riechorgan.

Ein *Gesichtsorgan* am Vorderhirn, wie es in primitiver Form bei Tuni-  
katen oder deren Larven noch vorkommt, ist bei *Amphioxus* verloren  
gegangen, wohl in Folge der Ausbildung noch mehr primitiver Sehorgane  
in mehr kaudalen Abschnitten des Neuralrohrs. Der Pigmentfleck des  
Vorderhirns kann wohl nicht als das Rudiment eines Kraniotenauges ange-  
sehen werden.

In Betreff des *Geruchsorgans* der Kranioten hat PETER (1901) die  
KUPFFERSche Hypothese der drei Riechplakoden: eine paarige und eine  
mediane, unpaare, wohl endgültig widerlegt. Bei den Amphirrhinen existiert  
keine unpaare Sinnesplakode. Die von v. KUPFFER dafür gehaltene Epithel-  
erhöhung ist ein Stauungswulst, der in der Endnaht beim Verschluss des  
schlitzförmigen Neuroporus auftritt.

Mit Unrecht aber spricht PETER dem *Amphioxus* ein Geruchsorgan ab,  
indem er sagt (1901, p. 6) dass derselbe „nicht mit einem solchen Organ  
ausgestattet ist“.

Die flimmernde Riechgrube wurde bekanntlich von KÖLLIKER (1843)  
entdeckt und auch als Riechorgan gedeutet. LANGERHANS (1876 p. 297)  
fand den unpaaren Riechnerv. Derselbe wurde später von einigen Autoren  
in Abrede gestellt. Er ist aber konstant vorhanden: Auf Querschnittserien  
von Ammoniumkarminpräparaten durch das ausgebildete Tier sehe ich den  
kurzen Nerv (wenn derselbe in ganzer Länge getroffen ist, auf einem  
einzigem Schnitt). Der Nerv tritt durch ein feines Loch in der rot gefärbten,  
ziemlich dicken Cutis als ein zarter, farb- und kernloser Faden aus dem  
Boden der Riechgrube, dann sich etwas verbreitend in das Vorderhirn.

Die Imprägnierung ist mir nicht gelungen; DOGIEL aber (1903 Taf. 24,  
Fig. 23. Nach der Beschreibung l.c. p. 195 ist statt Fig. 23, ein Druckfehler,  
Fig. 33 zu lesen) hat ihn mit Methylenblau und BOEKE (1908, p. 37) mit  
Silber imprägniert bekommen. Die Fibrillen des Nerven sind wohl als  
Ausläufer der Riechzellen am Boden der Grube aufzufassen, wie dies auch  
bei höheren Tieren der Fall ist.

Wie ich, HATSCHKE bestätigend, finde, entsteht die Grube durch Ein-  
senkung des medianen Neuroporus der Larve während der Metamorphose.  
Sie wird dann durch die Entwicklung des dorsalen Teiles der Schnauzen-  
flosse auf die linke Körperseite verschoben, während die Öffnung sich ver-  
schliesst. Der Zusammenhang des Bodens der Riechgrube mit dem Gehirn  
bleibt aber durch den feinen Riechnerv bestehen, der, obgleich auf die linke  
Seite gerückt, morphologisch median liegt. Man kann ihn deshalb auffassen  
als zusammengesetzt aus einem linken und rechten Fibrillenbündel, die bei  
höheren Tieren auseinander getreten sind in der Form eines paarigen Riech-  
nerven. Ähnliches gilt für die unpaare Plakode der Riechzellen am Boden  
der Grube.

In Betreff der Funktion beim ausgebildeten *Amphioxus* ist eine Beobach-  
tung von G. H. PARKER wichtig. Er schreibt (1908, p. 437): „This pit.....



was found in living animals to be lined with ciliated epithelium by the movement of which particles of carmine were carried into it from its *posterior* edge and discharged from it *anteriorly*."

Diese Beobachtung ergibt eine wichtige Analogie mit dem Geruchsorgan der Fische, bei denen ebenfalls ein durch Zilien hervorgerufener Wasserstrom dem Organ Riechpartikelchen zur Wahrnehmung herbeiführt.

Aus den angeführten Tatsachen folgt, dass man heutzutage keinen redlichen Grund mehr hat, das Vorhandensein eines Riechorgans bei *Amphioxus* zu bezweifeln.

Die Riechplakode mit dem Olfactorius bildet bei den Chordaten ein Organ *sui generis* das mit keinem anderen Sinnesorgan homologisiert werden kann. Es muss von chordalosen („wirbellosen") Vorfahren ererbt sein.

Einige Autoren wollen es mit den Seitenorganen zusammenstellen. Die Funktion derselben ist aber eine ganz andere, indem sie wellenförmige Erschütterungen im Wasser perzipieren. Eine Riechfunktion ist hier ausgeschlossen, da die schleimerfüllten Röhren keine Riechpartikelchen des umgebenden Wassers hineinlassen<sup>1)</sup>.

Aus welchen Organen bei Evertibraten oder deren Larven ist die Vorderhirnblase der Chordaten entstanden?

Die Tatsachen fehlen um diese Frage mit genügender Wahrscheinlichkeit beantworten zu können. Eine Vorstellung lässt sich allerdings machen. Die Enteropneusten kommen in erster Linie in Betracht.

Ich stelle mir nun vor, die Vorderhirnblase entstehe bei einer *Tornaria*-ähnlichen Larve aus der Einfaltung der Scheitelplatte, die sich durch das Zusammenkommen von zwei dorsalen Nähten (eine vordere Endnaht und eine hintere, die rostrale Fortsetzung der Rückenmarkснаht) zur Blase umbildet.

Am Vorderrande der Scheitelplatte<sup>2)</sup> lagen die Augenflecke (wie bei

<sup>1)</sup> Eine Zeitlang hat man die HATSCHESKEsche Grube des *Amphioxus* für ein Riechorgan gehalten. Diese Grube bildet einen der beiden Hauptteile des Präoralorgans; der andere Hauptteil ist das Geisselband, welches die Grube vorn und seitlich umgibt.

Ein Sinnesnerv fehlt und das ganze Organ entsteht aus dem Entoderm. HATSCHKE (1881) hat diese Entstehungsweise an Totalpräparaten wahrgenommen. Ich kann diese Wahrnehmung an Schnittserien bestätigen: nur finde ich dass das Geisselband nicht, wie HATSCHKE glaubt, die Grube allseitig umgibt, sondern stets einen (schliesslich schmalen) Teil des Hinterrandes derselben frei lässt. Aus diesem Hinterrand entsteht nach der Metamorphose die von mir (1901, Fig. 5, 6) so genannte Flimmergrube des ausgebildeten Tieres.

Mit Unrecht glaubt GOODRICH (1917), zwar ohne die Sache für bewiesen zu halten, dass das Geisselband aus dem Ektoderm stamme.

<sup>2)</sup> Die abortive Scheitelplatte einer *Tornaria* ist ungezweifelt in mancher Hinsicht zurückgebildet. Sie zeigt zwar noch Augenflecke, aber meines Wissens keine anderen Sinnesorgane, auch keine Hautnerven.

Bei der *Trochophora* anderer Achordaten (Evertibraten), wo die Scheitelplatte sich an der Bildung bleibender Kopfganglien beteiligt, hat man nicht nur Augenflecke, sondern auch andere Sinnesorgane und Hautnerven wahrgenommen.

Balanoglossuslarven). Hinter denselben strahlten, von den Seitenrändern der Platte, Hautnervenfibrillen aus in die Epidermis des Prosoma (Lobus präoralis). Hinter der Mitte der Platte, dem Seitenrande derselben unmittelbar angelagert, befand sich das paarige Riechfeld, durch Fibrillen der Riechzellen (N. olfactorius) mit dem Rande der Platte verbunden.

Bei der Umbildung der Scheitelplatte zur Vorderhirnblase lieferten die Augenflecke die Anlagen zu den paarigen Augen der Blase.

Die Hautnervenfibrillen sammelten sich zum N. terminalis.

Die paarigen Plakoden des Riechfeldes kamen in der dorsalen Medianlinie mit einander in Berührung und bildeten so die unpaare Plakode<sup>1)</sup> des Amphioxus. *Mutatis mutandis* gilt dasselbe für die Bildung der unpaaren Riechnerven. Die Monorrhinie des Amphioxus ist demnach als eine verkappte Amphirrhinie aufzufassen.

Man muss fragen, weshalb das N. terminalis nicht auch unpaar wurde und kann annehmen, dass sich hier Zellen der Endnaht (die hart vor den Augenflecken anfangend nach der Riechregion hinwächst) zwischen beide Nerven eingeschoben haben.

Das hintere Ende der Scheitelplatte unserer hypothetischen Larve muss sich fortgesetzt haben in denjenigen Teil der Neuralplatte aus welchem sich das Mittel- und Hinterhirn, sowie das Rückenmark bilden sollten.

Auch dieser Teil der Neuralplatte wurde rinnenförmig und schloss sich zum Rohre. Die Verschlussnaht trat etwa an der Grenze von Mittel- und Hinterhirn auf und wuchs vor- und rückwärts weiter. Ihr vorderes Ende beschränkte sich nicht auf das Mittelhirn, sondern trat auf den hinteren Teil der Scheitelplatte über, bis in die Gegend des Riechorgans, wo sie mit der Endnaht der Scheitelplatte zusammentraf.

Bei Balanoglossus kann man Andeutungen von diesem Teil der Neuralplatte erblicken im Kragenmark und dessen Fortsetzung in den dorsalen unpaaren Rumpfnerv<sup>2)</sup>:

Im Kragen (Mesoma) hat sich die Platte schon zum Neuralrohr (dessen Lumen obliteriert sein kann) geschlossen. Im Rumpfe (Metasoma) hat sich der dorsale Nerv mit dem aufliegenden Epithel noch nicht zum Rohre umgebildet.

Wenn diese Vorstellung richtig ist, so muss das Kragenmark ungefähr dem Mittelhirn der Vertebraten entsprechen (vielleicht gehört ein kleiner, vorderer Teil des Hinterhirns noch zum Kragenmark).

Der ventrale, unpaare Rumpfnerv kann nach dieser Vorstellung nicht als ein Vorläufer des Zentralnervensystems der Kranioten betrachtet werden.

1) Eine unpaare, mediane Riechplakode, etwa am Hinterrande der Scheitelplatte, kann die hypothetische Larve nicht gehabt haben. Dieselbe müsste der Neuralrinne aufgelagert gewesen sein und wäre bei der Umbildung der Rinne zum Neuralrohr in das Innere desselben hineingeraten.

2) Bei Balanoglossus verodet das Vorderhirn schon während der Metamorphose der Larve; bei den Tunikaten ist es mehr oder weniger degeneriert. Bei Amphioxus hat es das Gesichtsorgan verloren. Bei Kranioten aber kommt es zu hoher Entwicklung.

Ich halte ihn für einen ursprünglich paarigen, peripheren Nerv, der am hinteren Ende des Kragenmarks hervortritt, in den hinteren Ringrand des Kragens ventralwärts wächst, bis er in der ventralen Medianlinie den Nerv der anderen Körperseite erreicht, und mit diesem zum unpaaren, ventralen Rumpfnerven zusammentritt. Derselbe wuchs darauf in der ventralen Medianlinie des Rumpfes weiter rückwärts.

*(Die Literaturliste folgt in einer späteren, den Schluss der Riechorgans enthaltenden Mitteilung).*

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**Meteorology.** — *Earthquakes and Tides.* By S. W. VISSER. (Adj.-Director Meteorological Observatory at Batavia.)

(Communicated at the meeting of January 31, 1931).

1. In the year 1920 the civil officer of Amahei (South coast of Ceram, Moluccas) asked us whether there was any truth in the belief of the population that earthquakes occurred during ebb tide only.

Generally speaking this belief cannot be accepted, since such a simple fact would surely have been noticed long ago. Yet in this special case a relation between the two phenomena apparently exists as is shown in the next table <sup>1)</sup>.

Earthquakes near Amahei 1914—1919.

Hours after ebb	Number of earthquakes			Hours after ebb	Number of earthquakes		
	1914-'16	1917-'19	Total		1914-'16	1917-'19	Total
0—1	1	0	1	6—7	2	0	2
1—2	0	2	2	7—8	1	2	3
2—3	3	4	7	8—9	1	2	3
3—4	4	1	5	9—10	0	0	0
4—5	1	1	2	10—11	0	1	1
5—6	2	0	2	11—12	0	0	3
Totals . . .					15	16	31

The relation during both parts of the period investigated is evident, but contrary to the existing belief the earthquakes occurred some 2 or 3 hours after ebb tide.

2. During the month of August, 1930, an extraordinarily numerous series of eruptions of Mount Krakatau caused a great number of volcanic

<sup>1)</sup> Tide tables for Amahei are not available. The cotidal lines of the principal partial tides, however, show that the tides of Amahei coincide fairly well with those of Amboina (J. P. VAN DER STOK, *Elementaire theorie der getijden*, Kon. Ned. Med. Inst. Meded. N<sup>o</sup>. 8, Utrecht 1910). Moreover the harbour master of Saparoea (in the immediate neighbourhood of Amahei) observed the tides from November 11 to 18, 1920; the results confirmed the conclusion drawn from the cotidal lines.

earthquakes, which were registered from August 9—16 as faint disturbances by the horizontal Wiechert seismograph at Batavia. These disturbances coincided exactly with the period of severest volcanic activity. It was only rarely possible to read the individual phases. When possible, the distances deduced accorded correctly with the distance Krakatau-Batavia. When plotting the number of minutes of disturbed registration for each hour, an obvious period of about 12 hours during the latter part of the volcanic activity has been found, suggesting an influence of tides. Here too tide tables were not available and we had to use the tidal constants of Java's Fourth Point (Anjar Kidoel) at a distance of 40 km. Also in this case no considerable differences were to be expected.

The graphs (fig. 1) reveal a marked occurrence of volcanic earthquakes

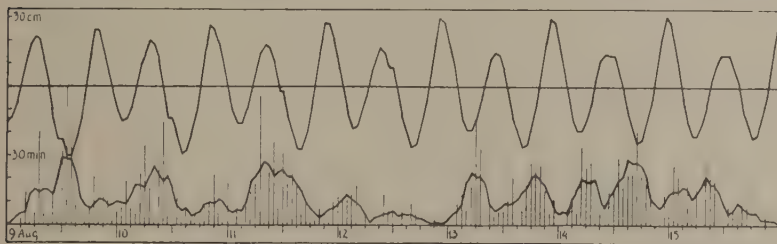


Fig. 1. Earthquakes and Tides, Krakatau.

during ebb-tide. The upper curve shows the tidal movement at Anjer Kidoel. The vertical lines give the number of minutes with seismic disturbance at Batavia for each hour, whereas the lower curve has been obtained by smoothing these hourly values. For this purpose overlapping means of each 5 subsequent hourly values were calculated.

During the first part the influence of tides on the seismic activity is absent, it develops on August 12 and is very evident from August 13—16. With each ebb the seismic activity increases. This phenomenon may be explained by the fact that the downward hydrostatic pressure counteracts the upward movements of the volcanic activity. That the effect was absent during the first part is explained by very strong volcanic activity or by its great depth, in both cases the influence of some two metres of water being negligible. We must presume a rather delicate balancing of both actions in order to get a periodical outlet of seismic activity.

3. It now appeared worth while to investigate the observation of the natives of Amahei more closely.

The research for Amahei-Saparoea was extended over the years 1914—1929. Moreover the earthquakes of Banda Neira (Moluccas), Padang (Westcoast of Sumatra) and Tjilatjap (Southcoast of Central Java) were investigated. For these three places good tidal constants are available. The method applied differed slightly from that of the year 1920 because the time indications in hours after ebb are insufficient to disclose the true



relation between the two phenomena, the time differences between ebb and flood amounting from 4 to 7 hours. Now the time between earthquake and ebb was expressed in the time between ebb and flood. The fraction obtained was taken negative when the earthquake occurred before the ebb, and positive when after. To make the results intercomparable all countings were expressed in percentages of the total number during the chosen period. Moreover smoothed curves were obtained by calculating overlapping means as described above for Krakatau.

The graphs, figures 2—5 show the results.

*Saparoëa* (Amahei) (fig. 2), 1914—1919; 27 earthquakes. Maximum during rising water, secondary maximum during falling water.

1920—1925; 36 earthquakes. The maximum during rising tide has disappeared; a poorly developed maximum before ebb is present.

1926—1927; no earthquakes.

1928—1929; 21 earthquakes. The effect is reversed: earthquakes occur with falling water.

This remarkable behaviour is to be explained by vertical movements of the earth's crust. Low water, low hydrostatic pressure promote the

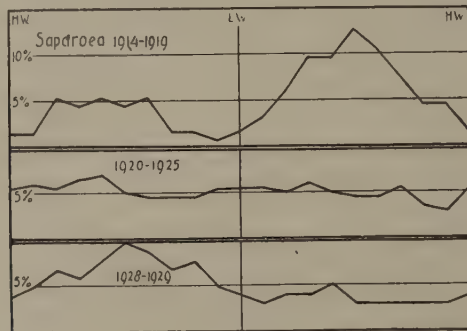


Fig. 2.

occurrence of earthquakes which are caused by a rising bottom. When earthquakes occur at high tide we may conclude that the bottom is sinking. Surely the correlation cannot be close: most earthquakes will occur independent of the fairly small changes of water pressure. Only when the earth's crust, because of increasing tectonic forces, becomes ripe for an earthquake the tide will influence the process. Evidently such cases are by no means rare.

The effect is complicated by the fact that the maxima of earthquake frequency do not coincide exactly with ebb or flood, but occur with rising or falling tide. Some amount of pressure may cause an earthquake, but then the stability of the earth's crust is re-established for some time and though the water is rising or falling still more no other earthquakes will occur. Therefore the earthquake-maximum precedes the acting tide. We have to expect that the rule holds for shallow earthquakes only.

We may conclude for Saparoza a rising of the bottom of the sea during 1914—1919 with some minor periods of sinking; then a quiet period from 1920—1925 (1927), followed by sinking in 1928 and 1929.

*Banda* (fig. 3. For Banda an excellent series of earthquake observations by the civil officer is available.

1914—1919; 47 earthquakes. Maximum during rising water.

1920—1925; 48 earthquakes showing some preference for falling water.

1926; two graphs based upon 36 and 38 earthquakes resp. Maximum between ebb and flood, but during the second part another maximum before ebb-tide has developed.

1927; 48 earthquakes; the maximum with rising tide is maintained.

1928 and 1929, three graphs, (60, 50 and 51 earthquakes resp.) show very clear maxima before the arrival of the ebb.

Here we find the same results as for Saparoza; a rising of the crust

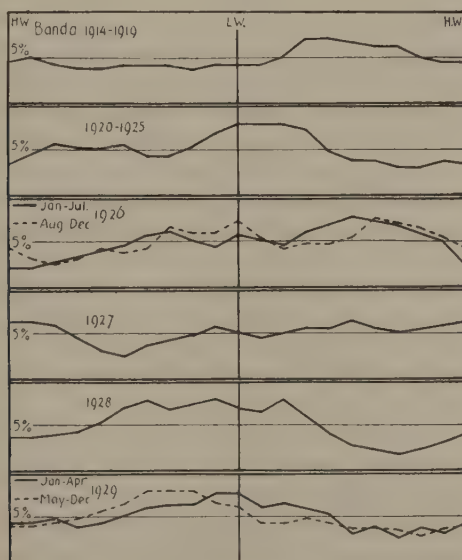


Fig. 3.

during 1914—1919; a sinking during 1928 and 1929. We find at Banda more particulars during the period 1920—1927 due probably to the much greater number of earthquakes (36 at Saparoza, 170 at Banda).

*Padang* (fig. 4). Padang had been chosen for this research because here since some years a rising of the sea was reported. Already in 1926 this fact was evident and the sea has continued to do so. Therefore a sinking of the coast had to be expected and the present investigations could give important information about this subject. The researches were made for the period 1914—July 1, 1930.

The number of earthquake reports for the 7 years 1914—1920 is small, viz. 35 in all, in 1920, however, amounting to 17. The graph for this year

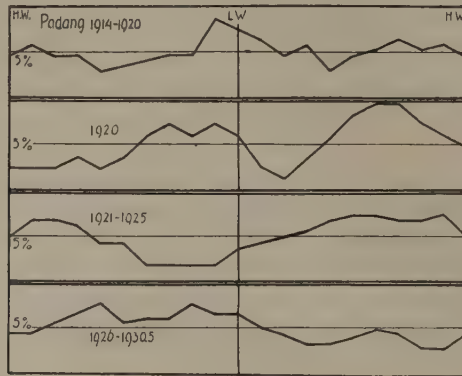


Fig. 4.

reveals the presence of a maximum during rising water, maintaining itself clearly during the years 1920—1925, but changing in 1926 to falling tide. Therefore we find indeed a sinking of the earth's crust from 1920—1925 incl. Since 1926 the coast seems to be rising again. We may expect that the crumbling of the coast will soon stop and that the danger for the town is past.

For Padang we may state that the conclusions drawn are confirmed by the facts.

*Tjilatjap* (fig. 5). The number of reports is small. For 1914 and 1915 no reports have been received. There is a clear antithesis between the years 1916—1924 (33 earthquakes) and 1925—1930.5 (29 earthquakes) a

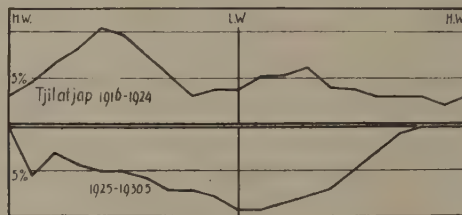


Fig. 5.

maximum with falling water during the first period followed by a maximum with rising water. Hence we may presume a rising of the coast followed by a sinking.

5. It seemed worth while to inquire from the population of the coast-districts for some more information about this phenomenon. The majority of answers received was negative. Generally earthquakes are ascribed to

neighbouring volcanos. Moreover some old legends are still extant: the earth is carried by a buffalo or a snake and a earthquake is caused when the animal shakes its head or its tail. As to Amahei, the present civil officer informed us, contrary to what his predecessor reported us in 1920, that the belief did not exist, but we have had positive answers now from East Ceram and the neighbouring island of Sorong at the most western point of New Guinea. In East Ceram earthquakes occur during rising tide, whereas in Sorong the belief is that earthquakes are strongest during ebb-tide. Earthquakes during rising tide also are reported from Kolonedale (East coast of SE peninsula of Celebes). At Badoeng (South-Bali) some fishermen believe that earthquakes occur only during falling tide (ebb). In the island of Sabang (Atjeh, Sumatra) the relation is known, but our reporter did not give any particulars.

In Tjilatjap (South Java) the population believes that an earthquake has occurred somewhere, when the sea is very high. This belief evidently refers to seismic tidal waves.

The natives of Waingapoe (Soemba, Lesser Soenda I.) maintain that the earth is a tree and the islands are the branches emerging out of the sea. When an earthquake occurs the branches are shaken and the sea rises. This legend too seems to refer rather to *t u n a m i s* than to the usual tides.

6. In the beginning of 1930 Japanese seismologists have found the same relation between earthquakes and tides<sup>1)</sup>. They write:

„For two months since the middle of February last, the watering town of Itô, Idu Province, had been shaken by incessant earthquakes that were counted by the thousands.”

„The shocks came generally in groups, at times as much as 80 in number in the short period of one hour, beginning activities coincident with low water and ending towards high water. In the present case the tide was indeed the dominant secondary cause. Towards the latter part of March, however, the connection has become less apparent, which fact coupled with the gradual increase in the average magnitude of shocks at the time, indicates a readier release of seismic energy. That low water enhanced seismic activity is in accord with the tilting of the so-called Itô-Kawana-block.”

E. TAMS<sup>2)</sup> has discussed researches on earthquake periodicities as caused by tides. He did not find evident relations. The investigators mentioned made use of great numbers of earthquakes during long time intervals and for different places. If, however, we have to do with a variable effect due to rather short intervals of rising and sinking, the result obtained in this way cannot be otherwise than negative.

*Observatory, Batavia, December 1930.*

<sup>1)</sup> A. IMAMURA, N. NASU, F. KISHINOUE and CH. YASUDA, On the recent Itô earthquakes, *Proc. Imp. Acad. Tokyo*. VI (1930) N<sup>o</sup>. 5, p. 190—193.

<sup>2)</sup> E. TAMS, Die Frage der Periodizität der Erdbeben, *Samml. geophys. Schriften*, Nr. 5, Berlin 1926, p. 54—58.

**Mathematics.** — *Sur quelques intégrales définies se rattachant aux fonctions de BESSEL. I.* Par J. G. RUTGERS. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of January 31, 1931).

§ 1. Nous trouvons déjà l'intégrale<sup>1)</sup>:

$$\int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^\nu \beta^\rho d\beta = \frac{\Gamma(\nu+1/2) \Gamma(\rho+1/2)}{\Gamma(\nu+\rho+1)} \cdot \frac{x^{\nu+\rho+1/2}}{\sqrt{2\pi}} I_{\nu+\rho+1/2}(x) \dots (1)$$

où  $\nu$  et  $\rho$  sont des nombres arbitraires, dont la partie réelle est plus grande que  $-\frac{1}{2}$ , ou abrégé:  $R(\nu) > -\frac{1}{2}$  et  $R(\rho) > -\frac{1}{2}$ .

Elle était une conséquence directe de l'identité:

$$\sum_{p=0}^s \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma)}{p! (s-p)!} = \frac{\Gamma(\mu) \Gamma(\sigma)}{\Gamma(\mu+\sigma)} \cdot \frac{\Gamma(s+\mu+\sigma)}{s!}, \dots (a)$$

qui fut trouvée d'une manière indirecte. Aussi on peut la démontrer par récurrence:

En remplaçant dans le premier membre de (a)  $s$  par  $s+1$  on trouve

$$\sum_{p=0}^{s+1} \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma+1)}{p! (s-p+1)!}$$

et en substituant:

$$\frac{1}{p! (s-p+1)!} = \frac{1}{s+1} \left\{ \frac{1}{(p-1)! (s-p+1)!} + \frac{1}{p! (s-p)!} \right\}$$

il suit:

$$\begin{aligned} & \sum_{p=0}^{s+1} \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma+1)}{p! (s-p+1)!} = \\ & = \frac{1}{s+1} \left\{ \sum_{p=1}^{s+1} \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma+1)}{(p-1)! (s-p+1)!} + \sum_{p=0}^s \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma+1)}{p! (s-p)!} \right\} = \\ & = \frac{1}{s+1} \left\{ \sum_{p=0}^s \frac{\Gamma(p+\mu+1) \Gamma(s-p+\sigma)}{p! (s-p)!} + \sum_{p=0}^s \frac{\Gamma(p+\mu) \Gamma(s-p+\sigma+1)}{p! (s-p)!} \right\}, \end{aligned}$$

où le dernier membre d'après (a) se réduit à:

$$\begin{aligned} & \frac{1}{s+1} \left\{ \frac{\Gamma(\mu+1) \Gamma(\sigma)}{\Gamma(\mu+\sigma+1)} \cdot \frac{\Gamma(s+\mu+\sigma+1)}{s!} + \frac{\Gamma(\mu) \Gamma(s+1)}{\Gamma(\mu+\sigma+1)} \cdot \frac{\Gamma(s+\mu+\sigma+1)}{s!} \right\} = \\ & = \frac{\Gamma(\mu) \Gamma(\sigma)}{\Gamma(\mu+\sigma+1)} \cdot \frac{\Gamma(s+\mu+\sigma+1)}{(s+1)!} (\mu+\sigma) = \frac{\Gamma(\mu) \Gamma(\sigma)}{\Gamma(\mu+\sigma)} \cdot \frac{\Gamma(s+\mu+\sigma+1)}{(s+1)!}, \end{aligned}$$

<sup>1)</sup> Nieuw Archief voor Wiskunde (2) VII, p. 400, (33).



d'où résulte que (a) est juste pour toute valeur (entière et positive) de  $s$ , parce qu'elle est juste pour  $s=0$  et  $s=1$ .

§ 2. D'abord nous y ajouterons quelques autres intégrales, dont la forme ne diffère qu'un peu de la précédente.

En introduisant pour les fonctions de BESSEL les séries infinies, qui sont absolument et uniformément convergentes, on peut effectuer les réductions suivantes:

$$\begin{aligned}
 a. \quad A_1 &= \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^\nu \beta^{\rho+1} d\beta = \\
 &= x^{\nu+\rho+2} \int_0^1 I_\nu(x(1-a)) I_\rho(xa) (1-a)^\nu a^{\rho+1} da = \\
 &= x^{\nu+\rho+2} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n! \Gamma(n+\nu+1)} \sum_{m=0}^{\infty} \frac{(-1)^m \left(\frac{x}{2}\right)^{2m+\rho}}{m! \Gamma(m+\rho+1)} \int_0^1 (1-a)^{2n+2\nu} a^{2m+2\rho+1} da = \\
 &= x^{\nu+\rho+2} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n! \Gamma(n+\nu+1)} \sum_{m=0}^{\infty} \frac{(-1)^m \left(\frac{x}{2}\right)^{2m+\rho}}{m! \Gamma(m+\rho+1)} \cdot \frac{\Gamma(2n+2\nu+1) \Gamma(2m+2\rho+2)}{\Gamma(2n+2m+2\nu+2\rho+3)}
 \end{aligned}$$

sous les conditions:  $R(\nu) > -\frac{1}{2}$  et  $R(\rho) > -1$ .

En appliquant la relation:

$$\Gamma(2z) = \frac{2^{2z-1}}{\sqrt{\pi}} \Gamma(z) \Gamma\left(z + \frac{1}{2}\right) \cdot \dots \cdot \dots \quad (b)$$

on trouve:

$$\begin{aligned}
 A_1 &= \frac{x^{\nu+\rho+2}}{2\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n!} \sum_{m=0}^{\infty} \frac{(-1)^m \left(\frac{x}{2}\right)^{2m+\rho}}{m!} \cdot \\
 &\quad \cdot \frac{\Gamma(n+\nu+\frac{1}{2}) \Gamma(m+\rho+\frac{3}{2})}{\Gamma(n+m+\nu+\rho+\frac{3}{2}) \Gamma(n+m+\nu+\rho+2)} = \\
 &= \frac{x^{\nu+\rho+2}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\rho+\frac{3}{2}) \Gamma(s+\nu+\rho+2)} \sum_{p=0}^s \frac{\Gamma(p+\nu+\frac{1}{2}) \Gamma(s-p+\rho+\frac{3}{2})}{p! (s-p)!}
 \end{aligned}$$

et donc d'après (a):

$$\begin{aligned}
 \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^\nu \beta^{\rho+1} d\beta &= \frac{\Gamma(\nu+\frac{1}{2}) \Gamma(\rho+\frac{3}{2})}{\Gamma(\nu+\rho+2)} \cdot \frac{x^{\nu+\rho+\frac{3}{2}}}{\sqrt{2\pi}} I_{\nu+\rho+\frac{1}{2}}(x), \quad \dots (2) \\
 R(\nu) &> -\frac{1}{2}, \quad R(\rho) > -1.
 \end{aligned}$$

Changeons  $\nu$  et  $\varrho$ , et de même  $x - \beta$  et  $\beta$  dans l'intégrale; alors nous trouvons:

$$\int_0^x I_\nu(x-\beta) I_\varrho(\beta) (x-\beta)^{\nu+1} \beta^\varrho d\beta = \frac{\Gamma(\nu+3/2) \Gamma(\varrho+1/2)}{\Gamma(\nu+\varrho+2)} \cdot \frac{x^{\nu+\varrho+3/2}}{\sqrt{2\pi}} I_{\nu+\varrho+1/2}(x), \dots (3)$$

$$R(\nu) > -1, R(\varrho) > -\frac{1}{2}.$$

La sommation de (2) et (3) nous donne (1).

b. Egalement on obtient:

$$\begin{aligned} A_2 &= \int_0^x I_\nu(x-\beta) I_\varrho(\beta) (x-\beta)^{\nu+1} \beta^{\varrho+1} d\beta = \\ &= x^{\nu+\varrho+3} \int_0^1 I_\nu(x(1-a)) I_\varrho(xa) (1-a)^{\nu+1} a^{\varrho+1} da = \\ &= x^{\nu+\varrho+3} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n! \Gamma(n+\nu+1)} \sum_{m=0}^{\infty} \frac{(-1)^m \left(\frac{x}{2}\right)^{2m+\varrho}}{m! \Gamma(m+\varrho+1)} \cdot \\ &\quad \cdot \frac{\Gamma(2n+2\nu+2) \Gamma(2m+2\varrho+2)}{\Gamma(2n+2m+2\nu+2\varrho+4)} = \\ &= \frac{x^{\nu+\varrho+3}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\varrho}}{\Gamma(s+\nu+\varrho+2) \Gamma(s+\nu+\varrho+5/2)} \sum_{p=0}^s \frac{\Gamma(p+\nu+3/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} = \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\varrho+3}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\varrho}}{s! \Gamma(s+\nu+\varrho+5/2)} \cdot (s+\nu+\varrho+2) = \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\varrho+3}}{2\sqrt{\pi}} \left\{ \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\varrho}}{s! \Gamma(s+\nu+\varrho+3/2)} + \right. \\ &\quad \left. + \frac{1}{2} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\varrho}}{s! \Gamma(s+\nu+\varrho+5/2)} \right\}, \end{aligned}$$

et donc:

$$\begin{aligned} \int_0^x I_\nu(x-\beta) I_\varrho(\beta) (x-\beta)^{\nu+1} \beta^{\varrho+1} d\beta &= \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\varrho+3/2}}{\sqrt{2\pi}} \left\{ I_{\nu+\varrho+1/2}(x) + \frac{1}{x} I_{\nu+\varrho+3/2}(x) \right\}, \dots (4) \\ R(\nu) &> -1, R(\varrho) > -1. \end{aligned}$$

c. Après des réductions conformes on obtient:

$$A_3 = \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^\nu \beta^{\rho+2} d\beta =$$

$$= \frac{x^{\nu+\rho+3}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\varrho+2) \Gamma(s+\nu+\varrho+5/2)}$$

$$\sum_{p=0}^s \frac{(s-p+\varrho+1) \Gamma(p+\nu+1/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!},$$

où la dernière somme peut être transformée ainsi:

$$\sum_{p=0}^s \frac{(s-p+\varrho+1) \Gamma(p+\nu+1/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} =$$

$$= (\varrho+1) \sum_{p=0}^s \frac{\Gamma(p+\nu+1/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} + \sum_{p=0}^{s-1} \frac{\Gamma(p+\nu+1/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p-1)!}.$$

En appliquant ensuite l'identité (a), on a:

$$A_3 = \frac{x^{\nu+\rho+3}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\varrho+2) \Gamma(s+\nu+\varrho+5/2)} \left\{ (\varrho+1) \frac{\Gamma(\nu+1/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+2)} \right.$$

$$\cdot \frac{\Gamma(s+\nu+\varrho+2)}{s!} + \frac{\Gamma(\nu+1/2) \Gamma(\varrho+5/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{\Gamma(s+\nu+\varrho+2)}{(s-1)!} \left. \right\} = \frac{\Gamma(\nu+1/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)}.$$

$$\frac{x^{\nu+\rho+3}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+5/2)} \left\{ (\varrho+3/2) (s+\nu+\varrho+3/2) - 1/2 (\nu+1/2) \right\} =$$

$$= \frac{\Gamma(\nu+1/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\rho+3}}{2\sqrt{\pi}} \left\{ (\varrho+\frac{3}{2}) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+3/2)} - \right.$$

$$\left. - \frac{1}{2} (\nu+\frac{1}{2}) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+5/2)} \right\},$$

donc:

$$\int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^\nu \beta^{\rho+2} d\beta =$$

$$= \frac{\Gamma(\nu+1/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\rho+5/2}}{\sqrt{2\pi}} \left\{ (\varrho+3/2) I_{\nu+\rho+1/2}(x) - \frac{\nu+1/2}{x} I_{\nu+\rho+3/2}(x) \right\}, \quad (5)$$

$$R(\nu) > -\frac{1}{2}, \quad R(\varrho) > -\frac{3}{2}.$$

En changeant de nouveau  $\nu$  et  $\varrho$ , et de même  $x - \beta$  et  $\beta$ , on trouve:

$$\left. \begin{aligned} & \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+2} \beta^\rho d\beta = \\ & = \frac{\Gamma(\nu+3/2) \Gamma(\varrho+1/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{x^{\nu+\rho+5/2}}{\sqrt{2\pi}} \left\{ (\nu+3/2) I_{\nu+\rho+1/2}(x) - \frac{\varrho+1/2}{x} I_{\nu+\rho+3/2}(x) \right\}, \\ & R(\nu) > -\frac{5}{8}, R(\varrho) > -\frac{1}{2}. \end{aligned} \right\} \quad (6)$$

d. Egalement nous trouvons:

$$\begin{aligned} A_4 &= \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+1} \beta^{\rho+2} d\beta = \\ &= \frac{x^{\nu+\rho+4}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\varrho+5/2) \Gamma(s+\nu+\varrho+3)} \\ &= \frac{x^{\nu+\rho+4}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\varrho+5/2) \Gamma(s+\nu+\varrho+3)} \left\{ (\varrho+1) \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \right. \\ &\quad \cdot \frac{\Gamma(s+\nu+\varrho+3)}{s!} + \frac{\Gamma(\nu+3/2) \Gamma(\varrho+5/2)}{\Gamma(\nu+\varrho+4)} \cdot \frac{\Gamma(s+\nu+\varrho+3)}{(s-1)!} \left. \right\} = \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+4)} \cdot \frac{x^{\nu+\rho+4}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+5/2)} \left\{ (\varrho+3/2) (s+\nu+\varrho+3/2) - \right. \\ &\quad \left. - 1/2 (\nu-2\varrho-3/2) \right\} = \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+4)} \cdot \frac{x^{\nu+\rho+4}}{2\sqrt{\pi}} \left\{ (\varrho+\frac{3}{2}) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+3/2)} - \right. \\ &\quad \left. - \frac{1}{2} (\nu-2\varrho-\frac{3}{2}) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{s! \Gamma(s+\nu+\varrho+5/2)} \right\}, \end{aligned}$$

donc:

$$\left. \begin{aligned} & \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+1} \beta^{\rho+2} d\beta = \\ & = \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+4)} \cdot \frac{x^{\nu+\rho+7/2}}{\sqrt{2\pi}} \left\{ (\varrho+\frac{3}{2}) I_{\nu+\rho+1/2}(x) - \frac{\nu-2\varrho-3/2}{x} I_{\nu+\rho+3/2}(x) \right\}, \\ & R(\nu) > -1, R(\varrho) > -\frac{3}{2}. \end{aligned} \right\} \quad (7)$$

En changeant  $\nu$  et  $\varrho$ , et de même  $x - \beta$  et  $\beta$ , on a :

$$\left. \begin{aligned} & \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+2} \beta^{\rho+1} d\beta = \\ & = \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+4)} \cdot \frac{x^{\nu+\varrho+7/2}}{\sqrt{2\pi}} \left\{ \left(\nu+\frac{3}{2}\right) I_{\nu+\varrho+1/2}(x) - \frac{\varrho-2\nu-3/2}{x} I_{\nu+\varrho+3/2}(x) \right\} \end{aligned} \right\} \quad (8)$$

$$R(\nu) > -\frac{3}{2}, \quad R(\varrho) > -1.$$

La somme de (7) et (8) nous donne (4).

e. Enfin nous calculons :

$$\begin{aligned} A_5 &= \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+2} \beta^{\rho+2} d\beta = \\ &= \frac{x^{\nu+\rho+5}}{2\sqrt{\pi}} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu+\rho}}{\Gamma(s+\nu+\varrho+3) \Gamma(s+\nu+\varrho+7/2)} \\ &\quad \sum_{p=0}^s \frac{(p+\nu+1)(s-p+\varrho+1) \Gamma(p+\nu+3/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} \end{aligned}$$

En divisant la dernière somme on trouve d'après (a) :

$$\begin{aligned} \sum_{p=0}^s \frac{(p+\nu+1)(s-p+\varrho+1) \Gamma(p+\nu+3/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} &= \\ &= \sum_{p=0}^s \frac{\Gamma(p+\nu+5/2) \Gamma(s-p+\varrho+5/2)}{p! (s-p)!} = \\ &= \frac{1}{2} (s+\nu+\varrho+5/2) \sum_{p=0}^s \frac{\Gamma(p+\nu+3/2) \Gamma(s-p+\varrho+3/2)}{p! (s-p)!} = \\ &= \frac{\Gamma(\nu+5/2) \Gamma(\varrho+5/2)}{\Gamma(\nu+\varrho+5)} \cdot \frac{\Gamma(s+\nu+\varrho+5)}{s!} = \\ &= \frac{1}{2} (s+\nu+\varrho+5/2) \cdot \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+3)} \cdot \frac{\Gamma(s+\nu+\varrho+3)}{s!} = \\ &= \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+5)} \cdot \frac{\Gamma(s+\nu+\varrho+3)}{s!} \{ (\nu+3/2)(\varrho+3/2)(s+\nu+\varrho+3/2)(s+\nu+\varrho+5/2) - \\ &\quad - \frac{1}{4} (\nu^2 - 4\nu\varrho + \varrho^2 - 2\nu - 2\varrho - 3/2)(s+\nu+\varrho+5/2) + \frac{3}{4} (\nu+3/2)(\varrho+3/2) \}, \end{aligned}$$

et ensuite :

$$\left. \begin{aligned} & \int_0^x I_\nu(x-\beta) I_\rho(\beta) (x-\beta)^{\nu+2} \beta^{\rho+2} d\beta = \\ & = \frac{\Gamma(\nu+3/2) \Gamma(\varrho+3/2)}{\Gamma(\nu+\varrho+5)} \cdot \frac{x^{\nu+\varrho+9/2}}{\sqrt{2\pi}} \left\{ (\nu+3/2)(\varrho+3/2) I_{\nu+\varrho+1/2}(x) - \right. \\ & \quad \left. - \frac{\nu^2-4\nu\varrho+\varrho^2-2\nu-2\varrho-3/2}{x} I_{\nu+\varrho+3/2}(x) + \frac{3(\nu+3/2)(\varrho+3/2)}{x^2} I_{\nu+\varrho+5/2}(x) \right\} \end{aligned} \right\} \quad (9)$$

$$R(\nu) > -\frac{3}{2}, \quad R(\varrho) > -\frac{3}{2}.$$



Il est évident qu'en continuant ainsi les résultats ne seront pas plus beaux.

§ 3. Au moyen des relations :

$$I_{-\frac{1}{2}}(y) = \sqrt{\frac{2}{\pi y}} \cos y \quad \text{et} \quad I_{\frac{1}{2}}(y) = \sqrt{\frac{2}{\pi y}} \sin y$$

on peut déduire des intégrales précédentes plusieurs autres d'une forme un peu plus simple.

En posant  $\varrho = 1/2$  dans la formule (1) on trouve :

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^\nu d\beta = \frac{x^{\nu+1}}{2\nu+1} I_{\nu+1}(x), \quad \{R(\nu) > -\frac{1}{2}\} \quad \dots (10)$$

En posant successivement  $\varrho = -1/2$  et  $\varrho = 1/2$  dans (2) on obtient respectivement :

$$\int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^\nu d\beta = \frac{x^{\nu+1}}{2\nu+1} I_\nu(x), \quad \{R(\nu) > -\frac{1}{2}\} \quad \dots (10a)$$

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^\nu \beta d\beta = \frac{2x^{\nu+2}}{(2\nu+1)(2\nu+3)} I_{\nu+1}(x), \quad \{R(\nu) > -\frac{1}{2}\} \quad \dots (11)$$

Ainsi  $\varrho = 1/2$  dans (3) nous donne :

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+1} d\beta = \frac{x^{\nu+2}}{2\nu+3} I_{\nu+1}(x), \quad \{R(\nu) > -1\} \quad \dots (12)$$

On déduit de (4) en substituant  $\varrho = -1/2$  et  $\varrho = 1/2$  respectivement :

$$\int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+1} d\beta = \frac{x^{\nu+2}}{2\nu+3} \left\{ I_\nu(x) + \frac{1}{x} I_{\nu+1}(x) \right\}, \quad \{R(\nu) > -1\} \quad \dots (12a)$$

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+1} \beta d\beta = \frac{2x^{\nu+3}}{(2\nu+3)(2\nu+5)} \left\{ I_{\nu+1}(x) + \frac{1}{x} I_{\nu+2}(x) \right\}, \quad \left\{ \begin{array}{l} \\ \{R(\nu) > -1\} \end{array} \right\} \quad (13)$$

En posant  $\varrho = -1/2$  resp.  $\varrho = 1/2$  dans (5) on obtient :

$$\int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^\nu \beta d\beta = \frac{2x^{\nu+2}}{(2\nu+1)(2\nu+3)} \left\{ I(x) - \frac{2\nu+1}{2x} I_{\nu+1}(x) \right\}, \quad \left\{ \begin{array}{l} \\ \{R(\nu) > -\frac{1}{2}\} \end{array} \right\} \quad (11a)$$

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^\nu \beta^2 d\beta = \frac{8x^{\nu+3}}{(2\nu+1)(2\nu+3)(2\nu+5)} \left\{ I_{\nu+1}(x) - \frac{2\nu+1}{4x} I_{\nu+2}(x) \right\}, \quad \left\{ \begin{array}{l} \\ \{R(\nu) > -\frac{1}{2}\} \end{array} \right\} \quad (14)$$

Ainsi  $\varrho = 1/2$  dans (6) nous donne :

$$\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+2} d\beta = \frac{x^{\nu+2}}{2\nu+5} \left\{ I_{\nu+1}(x) - \frac{2}{(2\nu+3)x} I_{\nu+2}(x) \right\}, \{R(\nu) > -\frac{3}{2}\}. \quad (15)$$

En posant  $\varrho = -1/2$  et  $\varrho = 1/2$  successivement dans (7), (8) et (9) on trouve respectivement :

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+1} \beta d\beta &= \\ &= \frac{2x^{\nu+3}}{(2\nu+3)(2\nu+5)} \left\{ I_\nu(x) - \frac{2\nu-1}{2x} I_{\nu+1}(x) \right\}, \{R(\nu) > -1\} \end{aligned} \quad (13a)$$

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+1} \beta^2 d\beta &= \\ &= \frac{8x^{\nu+4}}{(2\nu+3)(2\nu+5)(2\nu+7)} \left\{ I_{\nu+1}(x) - \frac{2\nu-5}{4x} I_{\nu+2}(x) \right\}, \{R(\nu) > -1\} \end{aligned} \quad (16)$$

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+2} d\beta &= \\ &= \frac{x^{\nu+3}}{2\nu+5} \left\{ I_\nu(x) + \frac{4(\nu+1)}{(2\nu+3)x} I_{\nu+1}(x) \right\}, \{R(\nu) > -\frac{3}{2}\} \end{aligned} \quad (15a)$$

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+2} \beta d\beta &= \\ &= \frac{2x^{\nu+4}}{(\nu+5)(2\nu+7)} \left\{ I_{\nu+1}(x) + \frac{2(2\nu+1)}{(2\nu+3)x} I_{\nu+2}(x) \right\}, \{R(\nu) > -\frac{3}{2}\} \end{aligned} \quad (17)$$

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+2} \beta^2 d\beta &= \\ &= \frac{2x^{\nu+4}}{(2\nu+5)(2\nu+7)} \left\{ I_\nu(x) - \frac{4\nu^2-1}{2(2\nu+3)x} I_{\nu+1}(x) + \frac{3}{x^2} I_{\nu+2}(x) \right\}, \{R(\nu) > -\frac{3}{2}\} \end{aligned} \quad (17a)$$

$$\begin{aligned} \int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+2} \beta^2 d\beta &= \\ &= \frac{8x^{\nu+5}}{(2\nu+5)(2\nu+7)(2\nu+9)} \left\{ I_{\nu+1}(x) - \frac{(2\nu-9)(2\nu+1)}{4(2\nu+3)x} I_{\nu+2}(x) + \frac{3}{x^2} I_{\nu+3}(x) \right\}, \{R(\nu) > -\frac{3}{2}\} \end{aligned} \quad (18)$$

§ 4. Nous compléterons le paragraphe précédent en calculant par la méthode directe les intégrales qui en certain sens sont les pendants de celles des formules (14), (16) et (18).

a. On trouve :

$$\begin{aligned}
 B_1 &= \int_0^x I_\nu (x-\beta) (\cos \beta) (x-\beta)^\nu \beta^2 d\beta = \\
 &= x^{\nu+3} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n! \Gamma(n+\nu+1)} \sum_{m=0}^{\infty} \frac{(-1)^m x^{2m}}{(2m)!} \int_0^1 (1-\alpha)^{2n+2\nu} \alpha^{2m+2} d\alpha = \\
 &= x^{\nu+3} \sum_{n=0}^{\infty} \frac{(-1)^n \left(\frac{x}{2}\right)^{2n+\nu}}{n! \Gamma(n+\nu+1)} \sum_{m=0}^{\infty} \frac{(-1)^m x^{2m}}{(2m)!} \cdot \frac{\Gamma(2n+2\nu+1) (2m+2)!}{\Gamma(2n+2m+2\nu+4)}, \{R(\nu) > -\frac{1}{2}\}
 \end{aligned}$$

donc d'après (b) et après une légère réduction :

$$B_1 = \frac{x^{\nu+3}}{2} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{\Gamma(s+\nu+2) \Gamma(s+\nu+5/2)} \sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+1/2)}{p!}.$$

En divisant la dernière somme de la manière suivante :

$$\begin{aligned}
 \sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+1/2)}{p!} &= (s+\nu+3/2)(s+\nu+1) \sum_{p=0}^s \frac{\Gamma(p+\nu+1/2)}{p!} - \\
 &- 2(s+\nu+1) \sum_{p=0}^s \frac{\Gamma(p+\nu+3/2)}{p!} + \sum_{p=0}^s \frac{\Gamma(p+\nu+5/2)}{p!} - \frac{3}{2} \sum_{p=0}^s \frac{\Gamma(p+\nu+3/2)}{p!},
 \end{aligned}$$

et d'après l'identité <sup>1)</sup> :

$$\sum_{p=0}^s \frac{\Gamma(p+\mu)}{p!} = \frac{\Gamma(s+\mu+1)}{\mu \cdot s!} \quad \dots \quad (c)$$

on trouve :

$$\begin{aligned}
 \sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+1/2)}{p!} &= \frac{(s+\nu+1) \Gamma(s+\nu+5/2)}{(\nu+1/2) \cdot s!} - \\
 &- \frac{2(s+\nu+1) \Gamma(s+\nu+5/2)}{(\nu+3/2) \cdot s!} + \frac{\Gamma(s+\nu+7/2)}{(\nu+5/2) \cdot s!} - \frac{3 \Gamma(s+\nu+5/2)}{2(\nu+3/2) \cdot s!} = \left\{ \dots \right. \quad (a) \\
 &= \frac{\Gamma(s+\nu+5/2)}{(\nu+1/2)(\nu+3/2)(\nu+5/2) \cdot s!} \left\{ 2(s+\nu+1) - \frac{3}{2}(\nu+\frac{1}{2}) \right\}
 \end{aligned}$$

donc :

$$B_1 = \frac{x^{\nu+3}}{(\nu+1/2)(\nu+3/2)(\nu+5/2)} \left\{ \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+1)} - \frac{3}{2}(2\nu+1) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+2)} \right\}$$

et ensuite :

$$\begin{aligned}
 \int_0^x I_\nu (x-\beta) (\cos \beta) (x-\beta)^\nu \beta^2 d\beta &= \\
 &= \frac{8 x^{\nu+3}}{(2\nu+1)(2\nu+3)(2\nu+5)} \left\{ I_\nu (x) - \frac{3(2\nu+1)}{4x} I_{\nu+1} (x) \right\}, \{R(\nu) > -\frac{1}{2}\} \quad (14a)
 \end{aligned}$$

<sup>1)</sup> Elle suit de (a) en y posant  $\sigma = 1$  ; de même on peut la démontrer par récurrence.

b. Egalement on trouve:

$$B_2 = \int_0^x I_\nu (x-\beta) (\cos \beta) (x-\beta)^{\nu+1} \beta^2 d\beta = \frac{x^{\nu+4}}{2} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{\Gamma(s+\nu+3) \Gamma(s+\nu+5/2)}$$

$$\sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+3/2)}{p!}, \{R(\nu) > -1\}$$

où d'après (a):

$$\sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+3/2)}{p!} =$$

$$= \frac{\Gamma(s+\nu+7/2)}{(\nu+3/2)(\nu+5/2)(\nu+7/2) \cdot s!} \{2(s+\nu+2) - \frac{3}{2}(\nu+\frac{3}{2})\} = \frac{\Gamma(s+\nu+5/2)}{(\nu+3/2)(\nu+5/2)(\nu+7/2) \cdot s!} \cdot$$

$$\cdot \{2(s+\nu+2)(s+\nu+1) - \frac{3}{4}(2\nu-1)(s+\nu+2) - \frac{3}{4}(\nu+\frac{3}{2})\};$$

donc il y a:

$$B_2 = \frac{x^{\nu+4}}{(\nu+3/2)(\nu+5/2)(\nu+7/2)} \left\{ \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+1)} - \right.$$

$$\left. - \frac{3}{8}(2\nu-1) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+2)} - \frac{3}{8}(\nu+\frac{3}{2}) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+3)} \right\},$$

et ensuite:

$$\int_0^x I_\nu (x-\beta) (\cos \beta) (x-\beta)^{\nu+1} \beta^2 d\beta =$$

$$= \frac{8x^{\nu+4}}{(2\nu+3)(2\nu+5)(2\nu+7)} \left\{ I_\nu (x) - \frac{3(2\nu-1)}{4x} I_{\nu+1}(x) - \frac{3(2\nu+3)}{4x^2} I_{\nu+2}(x) \right\}, \quad (16a)$$

$$\{R(\nu) > -1\}$$

c. Il nous reste:

$$B_3 = \int_0^x I_\nu (x-\beta) (\cos \beta) (x-\beta)^{\nu+2} \beta^2 d\beta =$$

$$= \frac{x^{\nu+5}}{2} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{\Gamma(s+\nu+3) \Gamma(s+\nu+7/2)} \sum_{p=0}^s \frac{(p+\nu+1)(s-p+1)(s-p+1/2) \Gamma(p+\nu+3/2)}{p!}$$

sous la condition:  $R(\nu) > -3/2$ , où la dernière somme, après division, se réduit d'après (a) de la manière suivante:

$$\sum_{p=0}^s \frac{(p+\nu+1)(s-p+1)(s-p+1/2) \Gamma(p+\nu+3/2)}{p!} =$$

$$= \sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+5/2)}{p!} - \frac{1}{2} \sum_{p=0}^s \frac{(s-p+1)(s-p+1/2) \Gamma(p+\nu+3/2)}{p!} =$$

$$\begin{aligned}
&= \frac{\Gamma(s+\nu+\frac{9}{2})}{(\nu+\frac{5}{2})(\nu+\frac{7}{2})(\nu+\frac{9}{2})s!} \left\{ 2(s+\nu+3) - \frac{3}{2}(\nu+\frac{5}{2}) \right\} - \\
&\quad - \frac{\Gamma(s+\nu+\frac{7}{2})}{2(s+\frac{3}{2})(\nu+\frac{5}{2})(\nu+\frac{7}{2})s!} \left\{ 2(s+\nu+2) - \frac{3}{2}(\nu+\frac{3}{2}) \right\} = \\
&= \frac{\Gamma(s+\nu+\frac{7}{2})}{(\nu+\frac{5}{2})(\nu+\frac{7}{2})(\nu+\frac{9}{2})s!} \left\{ 2(s+\nu+2)(s+\nu+1) - \frac{3(4\nu^2-1)(s+\nu+2)}{8(\nu+\frac{3}{2})} - \right. \\
&\quad \left. - \frac{3}{4}(2\nu-1) \right\}.
\end{aligned}$$

On trouve donc :

$$\begin{aligned}
B_3 = \frac{x^{\nu+5}}{(\nu+\frac{5}{2})(\nu+\frac{7}{2})(\nu+\frac{9}{2})} &\left\{ \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+1)} - \right. \\
&- \frac{3(4\nu^2-1)}{16(\nu+\frac{3}{2})} \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+2)} - \frac{3}{8}(2\nu-1) \sum_{s=0}^{\infty} \frac{(-1)^s \left(\frac{x}{2}\right)^{2s+\nu}}{s! \Gamma(s+\nu+3)} \left. \right\}.
\end{aligned}$$

et ensuite :

$$\begin{aligned}
&\int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+2} \beta^2 d\beta = \\
&= \frac{8x^{\nu+5}}{(2\nu+5)(2\nu+7)(2\nu+9)} \left\{ I_\nu(x) - \frac{3(4\nu^2-1)}{4(2\nu+3)x} I_{\nu+1}(x) - \frac{3(2\nu-1)}{2x^2} I_{\nu+2}(x) \right\}, \quad (18a) \\
&\quad \{R(\nu) > -\frac{3}{2}\}
\end{aligned}$$

§ 5. On peut encore déduire des intégrales précédentes les suivantes.

a. En multipliant les deux membres de (15) resp. (15a) avec  $x$  on trouve après soustraction de (17) resp. (17a) :

$$\begin{aligned}
&\int_0^x I_\nu(x-\beta) (\sin \beta) (x-\beta)^{\nu+3} d\beta = \\
&= \frac{x^{\nu+4}}{2\nu+7} \left\{ I_{\nu+1}(x) - \frac{6}{(2\nu+5)x} I_{\nu+2}(x) \right\}, \quad \{R(\nu) > -2\}. \quad (19)
\end{aligned}$$

$$\begin{aligned}
&\int_0^x I_\nu(x-\beta) (\cos \beta) (x-\beta)^{\nu+3} d\beta = \frac{x^{\nu+4}}{2\nu+7} \left\{ I_\nu(x) + \frac{3(2\nu+3)}{(2\nu+5)x} I_{\nu+1}(x) - \right. \\
&\quad \left. - \frac{6}{(2\nu+5)x^2} I_{\nu+2}(x) \right\}, \quad \{R(\nu) > -2\} \quad (19a)
\end{aligned}$$



b. De même en composant  $x^2 \times (15) - 2x \times (17) + (18)$  resp.  $x^2 \times (15a) - 2x \times (17a) + (18a)$  on obtient :

$$\int_0^x I_\nu(x-\beta)(\sin \beta)(x-\beta)^{\nu+4} d\beta = \frac{x^{\nu+5}}{2\nu+9} \left\{ I_{\nu+1}(x) - \frac{12}{(2\nu+7)x} I_{\nu+2}(x) + \right. \\ \left. + \frac{24}{(2\nu+5)(2\nu+7)x^2} I_{\nu+3}(x) \right\}, \{R(\nu) > -\frac{5}{2}\} \quad (20)$$

$$\int_0^x I_\nu(x-\beta)(\cos \beta)(x-\beta)^{\nu+4} d\beta = \frac{x^{\nu+5}}{2\nu+9} \left\{ I_\nu(x) + \frac{8(\nu+2)}{(2\nu+7)x} I_{\nu+1}(x) - \right. \\ \left. - \frac{48(\nu+2)}{(2\nu+5)(2\nu+7)x^2} I_{\nu+2}(x) \right\}, \{R(\nu) > -\frac{5}{2}\} \quad (20a)$$

**Chemistry.** — *Untersuchungen über den Einfluss intensiver Trocknung auf die Einstellung des inneren Gleichgewichts.* Von A. SMITS, E. L. SWART, P. BRUIN und W. M. MAZEE. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of January 31, 1931).

Wie in der Abhandlung „Allotropie und inneres Gleichgewicht“<sup>1)</sup> auseinander gesetzt worden ist, wurden die von dem Ehepaar BAKER bei intensiv getrocknetem Stickstofftrioxyd<sup>2)</sup> und von BAKER<sup>3)</sup> bei 10 anderen intensiv getrockneten Flüssigkeiten gefundenen Siedepunkterhöhungen und auch die Zunahme der Dampfdichte durch die von der Theorie der Allotropie angenommene Komplexität jedes sogenannten einfachen Stoffes erklärt. Es wurde zwar erst an eine Überhitzung gedacht; weil aber in den Fällen, wo die Siedetemperatur 30°—60° erhöht gefunden wurde, das Sieden nach BAKER ebenso ruhig stattfand wie beim normalen Siedepunkt und Kontakt mit getrockneter, doch nicht intensiv getrockneter Luft nach einiger Zeit wieder ein Sinken der Siedetemperatur bis zur normalen Höhe verursachte, bekamen wir den Eindruck, dass obwohl eine gewisse Überhitzung natürlich nicht ausgeschlossen war, das Hauptphänomen ein anderes war. Dabei kam noch, dass BAKER parallel gehende Effekte bei der Bestimmung der Oberflächenspannung und der Dampfdichte fand. Ein Siede-Experiment zusammen mit BAKER und ein anderes in Amsterdam ausgeführt<sup>4)</sup>, führten qualitativ zu demselben Resultat und so wurde der Zweifel, welcher sich immer wieder erhoben hatte, einige Zeit zu schweigen gebracht. Lange dauerte das aber nicht; SMITS wollte eine Untersuchungsmethode anwenden, welche vollkommen einwandfrei war und wählte dafür die *Dampfspannungsbestimmung*. Indem er BAKER ersuchte wenigstens von einer intensiv getrockneten Flüssigkeit den Dampfdruck zu bestimmen, wurde in Amsterdam in 1923 mit dieser Methode angefangen<sup>5)</sup>. BAKER fand den Dampfdruck von intensiv getrocknetem Äthyläther bei 20° ungefähr 68 mm Hg niedriger als bei der feuchten Flüssigkeit. Das Resultat von unseren eigenen ersten Versuchen war, dass der Dampfdruck von vorher gut getrockneten Flüssigkeiten nach intensiver Trocknung sich einigermaßen ändert, d.h. meistens ein wenig abnahm und bei Destillation das Destillat einen etwas höheren Dampfdruck zeigte als der Rest. Es schien also, dass das innere Gleichgewicht durch die intensive Trocknung ein wenig verschoben war und die Flüssigkeit sich bei der Destillation wie ein Gemisch verhielt, sodass man zu dem Schluss kam, dass die innere

<sup>1)</sup> Z. f. Phys. Chem., **129**, 33 (1927).

<sup>2)</sup> Trans. Chem. Soc., **51**, 2339 (1912).

<sup>3)</sup> Trans. Chem. Soc., **121**, 568 (1922).

<sup>4)</sup> Trans. Chem. Soc., **125**, 1068 (1924).

<sup>5)</sup> J. Chem. Soc. (1924), 1068.

Gleichgewichtseinstellung merkbar gehemmt worden war<sup>1)</sup>). Nun waren aber die gefundenen Effekte viel zu schwach um die von BAKER konstatierten grossen Siedepunkterhöhungen zu erklären und so schien es immer wahrscheinlicher, dass ein grosser Teil der BAKERSchen Siedepunkterhöhungen einer Überhitzung zuzuschreiben war; aber dann blieben doch noch die merkwürdigen Resultate der Oberflächenspannungen und der Dampfdichtebestimmungen zu erklären. Was die Siedepunktsbestimmungen anbelangt, trat Juni 1928 eine neue Phase ein, als wir bei Wiederholung eines Experimentes von BAKER, zum Studium des Einflusses eines elektrischen Feldes auf den Siedepunkt<sup>2)</sup>, fanden, dass feuchtes Benzol, nachdem es einige Zeit einem elektrischen Felde unterworfen gewesen war, bei Erhitzung in einem Flüssigkeitsbad erst bei  $95^{\circ}$  anfang zu sieden und dann regelmässig weiter siedete bei  $88^{\circ}$ , während vor der Anwendung des elektrischen Feldes der Siedepunkt  $80.5^{\circ}$  war. Erhitzten wir dann aber dieselbe Flüssigkeit nicht mittelst eines Flüssigkeitsbades, doch sehr lokal von der Seite mit einem Mikrobrenner, so siedete die Flüssigkeit wieder bei  $80.5^{\circ}$ . Hieraus folgte also, dass unter den Einfluss eines elektrischen Feldes das Benzol eine Änderung erfahren hatte, wodurch es in einem Flüssigkeitsbad erhitzt  $8^{\circ}$  höher siedete als zuvor, während bei Erhitzung mit dem Mikrobrenner der Siedepunkt normal gefunden wurde. Daraus wurde geschlossen<sup>3)</sup>, dass das Benzol in dem elektrischen Felde wahrscheinlich staubfrei geworden war, wodurch das Auftreten einer Überhitzung leichter stattfindet. Weil die lokale Erhitzung von der Seite mittelst eines Mikrobrenners die Überhitzung zu einem Minimum zu reduzieren vermag, wurde bei dieser Erhitzungsmethode der normale Siedepunkt gefunden. Es leuchtet ein, dass dieser Befund die grossen, von BAKER gefundenen Siedepunkterhöhungen in ein anderes Licht stellte, wenn man nämlich die nicht unwahrscheinliche Annahme macht, dass Flüssigkeiten in Kontakt mit  $P_2O_5$ , schliesslich staubfrei werden. In diesem fall würde man dann Flüssigkeiten bekommen, die, im Flüssigkeitsbade erhitzt, eine grosse Überhitzung zeigen können<sup>4)</sup>. Es wurde denn auch in der eben referierten Abhandlung (1928) folgendes bemerkt: "Now it is known that the most favourable condition for superheating is to heat in a bath and the best way to prevent superheating is to heat with a small flame applied at the point on the bulb, containing the liquid. When heating was effected in the latter way with application of the electrical field, the benzene boiled at  $80.5^{\circ}$  and the phenomenon mentioned by BAKER had disappeared completely, thus showing that his high boiling points may be affected to an unknown degree by superheating." Es ist klar, dass wenn man sich auf den Standpunkt stellt, dass hier nur von Überhitzung die Rede war, auch in unserem Experiment, bei dem Zerschlagen des Abschlitzröhrchens, der Staub, der

<sup>1)</sup> J. Chem. Soc. (1926), 2655.

<sup>2)</sup> J. Chem. Soc. (1928), 1055.

<sup>3)</sup> J. Chem. Soc. (1928), 2399.

<sup>4)</sup> In der Abhandlung J. Chem. Soc. (1928), 2400, wurde schon darauf hingewiesen.

mit der Luft in das Apparat trat, die Ursache des Aufhebens der Siedepunktserhöhung gewesen sein muss. Im Allgemeinen musste dann auch bei allen Versuchen BAKERS der Rückkehr des normalen Siedepunktes, also auch bei seinem Experiment mit  $\text{N}_2\text{O}_3$ , dem Staub zugeschrieben werden.

Hiermit ist dann aber noch nichts gesagt über das WESEN der Staubwirkung. Es ist bekannt wie stark die katalytische Wirkung von Staub für verschiedene Reaktionen ist und so könnte man hier fragen ob vielleicht Staub auch die Einstellung des inneren Gleichgewichts beschleunigt. — Man kann die Möglichkeit dieser Wirkung natürlich nicht sofort verneinen, und in diesem Fall würden die von BAKER gefundenen Siedepunktserhöhungen eine sehr besondere Bedeutung haben, doch wenn dem so ist muss eine vollkommen staubfreie Flüssigkeit bei vorsichtiger Oberflächenverdampfung einen zu niedrigen Druck zeigen. — Es sind schon vor einigen Monaten Versuche zur Beantwortung dieser Frage angefangen.

Was die Resultate bei der Bestimmung der Oberflächenspannung anbelangt, diese scheinen nicht mehr als eine Stütze der Siedepunktserhöhungen betrachtet werden zu können, seit BAKER bei dem Benzol, das einem elektrischen Felde unterworfen war, eine abnormale Oberflächenspannung fand, während wir konstatierten, dass der Siedepunkt, mit dem Mikrobrenner bestimmt, normal war<sup>1)</sup>. Es bleiben also nur noch die Dampfdichtebestimmungen BAKERS, welche die von ihm gefundenen Siedepunktserhöhungen zu stützen scheinen. Inzwischen zeigte SMITS, dass sich aus den Siedepunktsbestimmungen BAKERS schliessen lässt, dass die intensive Trocknung höchstens eine Verzögerung der inneren Gleichgewichtseinstellung bewirkt und dass in Zusammenhang hiermit Effekte könnten erwartet werden bei solchen Phänomenen, welche zu den „Geschwindigkeitsphänomenen“ gehören, wie rasche Temperaturänderungen, schnelle Verdampfung und Destillation<sup>2)</sup>. — Effekte würden also auch auftreten können bei der Dampfdichtebestimmung nach der Methode von VICTOR MEYER.

Während wir unsere Versuche über den Einfluss intensiver Trocknung auf den Dampfdruck fortsetzten, stiessen wir auf verschiedene Schwierigkeiten. Es stellte sich heraus, dass Destillationsversuche, ausgeführt mit Apparaten, welche viel  $\text{P}_2\text{O}_5$  enthielten, nicht ganz zu vertrauen sind, weil, wenn das Gefäss mit  $\text{P}_2\text{O}_5$  auch ein wenig Flüssigkeit enthält, das  $\text{P}_2\text{O}_5$  durch die verdampfende Flüssigkeit abgekühlt werden kann. Und weil das pulverige  $\text{P}_2\text{O}_5$  die Wärme schlecht leitet, wird es lange dauern bevor diese Masse die Temperatur des Bades angenommen hat<sup>3)</sup>. Es müssen also die früheren Untersuchungen wiederholt werden mit einem Thermometer in der  $\text{P}_2\text{O}_5$  Masse oder die Kugel mit  $\text{P}_2\text{O}_5$  soll immer eine höhere Temperatur besitzen als der übrige Teil des Apparates, oder man muss mit kleineren Quantitäten  $\text{P}_2\text{O}_5$  arbeiten<sup>4)</sup>.

<sup>1)</sup> l. c.

<sup>2)</sup> l. c.

<sup>3)</sup> J. Chem. Soc. (1929), 2712.

<sup>4)</sup> Z. f. Phys. Chem., 129, 33 (1927).



Es stellte sich heraus, dass eine Wiederholung unserer Versuche wegen einer anderen Schwierigkeit, welche noch viel wichtiger war, absolut notwendig schien. Um unsere Flüssigkeiten luftfrei zu machen, hatten wir immer, wie allgemein gebräuchlich, das Gefäß unseres Dampfdruckapparates, welches mit der Flüssigkeit gefüllt war, in flüssiger Luft abgekühlt und das Apparat dann bis zu  $10^{-6}$  mm Hg evakuiert. Danach wurde dann die Verbindung mit der Pumpe unterbrochen und die feste Masse durch vorsichtige Erwärmung geschmolzen. Dann wurde das Gefäß wieder in flüssige Luft gebracht und aufs neue hoch evakuiert u.s.w. Die Manipulation wurde drei oder vier Mal wiederholt. Weil wir aber schliesslich diese Methode nicht ganz vertrauten, entschlossen wir uns zu untersuchen ob sie wirklich zum Ziel führte. Wir wandten dazu einen Apparat an, welches eine Modifikation des Apparates ist, dass SMITS für TERWEN in 1913 zur Prüfung des von ihm bereiteten Cyans anfertigen liess <sup>1)</sup>. Dieser Apparat ist eine Kombination eines Differentialmanometers, von einem Quecksilberdampfdruckindikator versehen, mit einem Destillationsapparat.

Mit diesem Apparat erhielten wir das unerwartete Resultat, dass die immer angewandte Methode für das Gasfrei-machen von Flüssigkeiten *absolut* ungenügend war, denn es stellte sich heraus, dass bei dieser Methode noch so viel Gas (Luft) zurück bleiben konnte, dass die Genauigkeit der Dampfdruckbestimmungen dadurch stark beeinflusst wurde. Es stellte sich heraus, dass die gefundenen Effekte bei den Destillationsversuchen durch die Gasreste verursacht sein könnten <sup>2)</sup> und dass wir also gezwungen waren diese Versuche mit vollkommen gasfreien Flüssigkeiten zu wiederholen.

Mit dem obengenannten Apparat haben wir dann eine neue Methode ausgearbeitet um vollkommen gasfreie Flüssigkeiten herzustellen <sup>3)</sup>. Für die neuen Untersuchungen wurden Apparate angefertigt mit Glasfederindikatoren und von Glasventilen versehen, welche so fein geschliffen waren, dass sie ohne Hahnfett sehr genügend schlossen.

Diese Apparate wurden mit Flüssigkeiten gefüllt, welche nach unserer Methode gasfrei gemacht waren. Einige dieser enthalten Gefässe mit feinem kristallisiertem reinem Phosphorpentoxyd, während die anderen Apparate Gefässe mit halb verflüssigtem Phosphorpentoxyd gefüllt besitzen. Das fein kristallisierte Phosphorpentoxyd war im Hochvakuum destilliert und das halb verflüssigte wurde im Hochvakuum bis zum Weichwerden des Glases erhitzt. So wurden also an einige Flüssigkeiten nach einer Methode, welche, unsrer Einsicht nach, nicht weiter verbessert werden kann, eine neue Reihe Dampfspannungen und Destillationsuntersuchungen ausgeführt. Die erste Bestimmung wurde sofort nach der Füllung und die anderen nach verschiedenen Perioden der intensiven Trocknung ausgeführt. Das Resultat ist, dass wir bis zu diesem Augenblick, nach acht Monaten intensiver Trocknung, keine Effekte haben konstatieren können und wir

<sup>1)</sup> Dissertation Amsterdam (1913). Z. f. Phys. Chem., **91**, 469 (1916).

<sup>2)</sup> Siehe Z. f. Phys. Chem., **129**, 33 (1927).

<sup>3)</sup> J. Chem. Soc. (1929), 2724.



haben dadurch den Eindruck bekommen, dass die früher konstatierten Effekte an Gasreste zugeschrieben werden müssten.

Dass die Phasen eines sogenannten einfachen Stoffes komplex sind, daran kann man kaum mehr zweifeln und es liegt auf der Hand zu erwarten, dass die inneren Umsetzungen in den flüssigen Phasen ebenso wie so viele andere Umsetzungen in Gasphasen durch intensive Trocknung verzögert werden können, aber vielleicht ist es bei Flüssigkeiten viel schwieriger. Ferner wird es natürlich von der Differenz zwischen den Dampfdrücken der aus verschiedenen Molekülararten bestehenden Pseudokomponenten abhängen, ob eine Verzögerung der inneren Umsetzungen sich durch unsere Dampfdruckmessungen kundgeben kann. Sehr merkwürdig ist es, dass die festen Phasen von P, von  $\text{SO}_3$  und von  $\text{P}_2\text{O}_5$  nach der selben Untersuchungsmethode so deutlich ihre Komplexität zeigten. Die Untersuchungen werden in verschiedener Richtung fortgesetzt durch Studium von *Geschwindigkeitsphänomenen*. So wird heute zum Beispiel auch der Einfluss der Geschwindigkeit der Kondensation auf die Kondensationswärme der Dämpfe untersucht.

### *Zusammenfassung.*

Zusammenfassend kommen wir also zu dem Schluss, dass, wie schon in 1928 dargetan wurde, die grossen von BAKER gefundenen Siedepunkterhöhungen an Überhitzung zugeschrieben werden müssen, welche Erscheinung bei seinen intensiv getrockneten Flüssigkeiten so stark zu Tage trat, weil diese Flüssigkeiten wahrscheinlich durch Kontakt mit  $\text{P}_2\text{O}_5$  staubfrei geworden waren, in welchem Fall bei Erwärmung *mittelst eines Flüssigkeitsbades* sehr leicht eine starke Überhitzung auftreten kann.

Die Staubwirkung könnte auch eine katalytische Wirkung sein für die innere Umwandlungen, welche für die Dampfbildung erforderlich sind, aber dann muss eine staubfreie Flüssigkeit bei Oberflächenverdampfung einen zu niedrigen Dampfdruck zeigen, welches jetzt untersucht wird.

Die Resultate bei den Dampfdruck- und Destillationsuntersuchungen erhalten, sind durch uns nachgeprüft und dabei sind noch Fehler entdeckt worden, welche die gefundenen Effekte hervorrufen konnten. Es wurde gefunden dass der Hauptfehler, ganz unerwartet, durch Gasreste in den untersuchten Flüssigkeiten verursacht wird. Nachdem eine Methode ausgearbeitet war um diesen Fehler vollkommen zu beseitigen, wurde eine neue Reihe Untersuchungen angefangen, wobei bis heute, nach acht Monaten intensiver Trocknung, noch keine Effekte konstatiert werden konnten. Die Untersuchungen werden fortgesetzt und man wird abwarten müssen, ob dieses negatives Resultat sich aufrecht erhält. In der nächsten Abhandlung wird unsere Methode zum gasfrei machen von Flüssigkeiten und unsere neuere Untersuchungsmethode beschrieben werden.

*Laboratorium für allgemeine und anorganische  
Chemie der Universität.*

*Amsterdam, Dezember 1930.*

**Chemistry.** — *Anacardic acid.* By A. J. HAAGEN SMIT. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated at the meeting of January 31, 1931).

In a communication on Minjak Pelandjau, the exudation from the wood of *Pentaspadon Motleyi* <sup>1)</sup>, attention was drawn to anacardic acid, which occurs in the fruit of *Anacardium occidentale*, and the suggestion was made that it may be related to pelandjauc acid.

By courtesy of Dr. LAM, the director of the Buitenzorg herbarium, Prof. VAN ROMBURGH received about 5 KGr. of that fruit from Java, which were put at my disposal for a study of the question on the structure of anacardic acid.

STÄDELER <sup>2)</sup> and RUHEMANN, SKINNER <sup>3)</sup> noted in the pericarp of the fruit of *Anacardium occidentale*, as well as in those of *Anacardium orientale* the presence of an acid. Analysis of the acid and its salts pointed to the formula  $C_{22}H_{32}O_3$  containing one carboxyl and one hydroxyl group.

Eighty fruits weighing 500 gr. had the edible kernel taken out and the skins (320 gr.) ground and extracted with ether. After evaporation of the ether, the residue was a yellow viscous liquid which turned red-brown with aqueous potassium hydroxide on exposure to the air; rapid coloration also took place if a little laccase was added, which is probably the reason why this oily substance is commonly described as red brown. A warm alcoholic solution of the residue was treated with freshly prepared lead hydroxide in order to convert the acid in its leadsalt. After having been cooled, the lead salt was filtered off and decomposed with sulfuric acid. In this way 40 gr. of crude anacardic acid was prepared. After repeating this procedure a slightly yellow coloured product was obtained, which on inoculation with pelandjauc acid, crystallised. This fact pointed to a relationship between these acids, but a small depression of the mixing melting point was noted. A difference in the position of the double linkages in the side chain could easily produce such a difference; it was therefore important to try to obtain the better crystallised tetrahydro-derivatives.

<sup>1)</sup> These Proc. **32**, 693 (1929); **33**, 589, 690 (1930).

<sup>2)</sup> A. **63**, 137 (1847).

<sup>3)</sup> B. **20**, 1861 (1887).

*Tetrahydro-anacardic acid.*

Anacardic acid was hydrogenated in ethylacetate solution with platinum-black as catalyst, two molecules of hydrogen were absorbed. The tetrahydro-product was recrystallised from diluted methylalcohol and from petroleum ether in which it is sparingly soluble in the cold. After several crystallisations the melting point remained at  $92^{\circ}$  and showed a depression of  $7^{\circ}$  with tetrahydro-pelandjaic acid, m. p.  $98^{\circ}$ .

Analysis: Found 75.98 % C. and 10.63 % H.

$C_{22}H_{36}O_3$  requires 75.79 % C. and 10.42 % H.

This tetrahydro-product gave a violet coloration with  $FeCl_3$  in alcoholic solution just like tetrahydro-pelandjaic acid, from which we conclude in this case also the presence of a hydroxyl and a carboxyl group in ortho-position.

*Decarboxylation of anacardic acid.*

Just like pelandjaic acid this substance loses carbon dioxide by heating at  $220^{\circ}$ . After heating during one hour the decarboxylation was complete and the remaining product was distilled at 0.4 mm. Boiling point  $205^{\circ}$ . The methyl ether of this phenolic product was prepared by shaking it with dimethyl sulfate and sodium hydroxide solution. It boiled at  $202^{\circ}$  (0.5 mm.). The determination of the methoxyl group gave negative results, proving that this ether is also remarkably resistant to the action of hydriodic acid.

$d_4^{15} = 0.9240$        $n_D^{15} = 1.5076$       Found:  $M_D = 101.3$ .

$C_{22}H_{38}O$  requires  $M_D = 100.9$ .

*Hydrogenation of the methyl ether of the phenol.*

1.5 grs were hydrogenated in 30 grs of ethyl acetate with platinum black. In twenty minutes the reduction stopped, the aromatic double linkages resisting further hydrogenation. This tetrahydro-product melted at  $30^{\circ}$ .

Analyse: Found: 82.64 % C and 12.35 % H.

$C_{22}H_{38}O$  requires 82.94 % C and 12.05 % H.

*Methyl tetrahydro anacardic methyl ester.*

By shaking the acid with dimethyl sulphate and sodium hydroxyde solution the ether-ester was prepared. Boiling point  $220-222^{\circ}$  (0.5 mm.),

Analysis: Found: 76.59 % C and 9.72 % H.

$C_{24}H_{36}O_3$  requires 77.23 % C and 9.75 % H.

Methoxyl determination: Found:  $OCH_3$  16.0 %.

$C_{21}H_{30}COOCH_3OCH_3$  requires:  $OCH_3$  16.67 %.

Hydrogenation of this ether-ester with platinum-black in ethyl acetate

produced the tetrahydro-derivative which crystallised from alcohol m.p.  $38^{\circ}$ .

Analysis: Found: 76.57 % C and 10.84 % H.

$C_{24}H_{40}O_3$  requires: 76.59 % C and 10.72 % H.

Methoxyl determination: Found:  $OCH_3$  16.59 %.

$C_{21}H_{34}COOCH_3OCH_3$  requires: 16.49 %  $OCH_3$ .

#### *Oxidation of the tetrahydro ether ester.*

1 gram oxidised with  $CrO_3$  in acetic acid yielded a crystalline acid, which precipitated when diluted with water. It proved to be insoluble in aqueous sodium hydroxide. After filtration of the sodium salt, this was transferred into the acid with sulfuric acid. After crystallisation from alcohol and from petroleum ether the melting point was raised to  $59^{\circ}$ . The substance gave no depression with palmitic acid, on the other hand melting point depressions were obtained with stearic acid and myristic acid.

From this result we conclude that a normal chain of 16 carbon atoms is present, in which no hydrogen is replaced by the carboxyl or hydroxyl group.

#### *Hydrogenation of the phenol $C_{21}H_{31}OH$ .*

The decarboxylation product of anacardic acid was hydrogenated with platinum oxide in acetic acid solution. After taking up 5 mols of hydrogen the reduction came to an end. After evaporating the solution a substance m.p.  $31^{\circ}$  could be obtained. This proved to be the dekahydro product.

Hydroxyl determination: Found: OH 5.74 %.

$C_{21}H_{41}OH$  requires 5.48 %.

#### *Dehydration of the phenol.*

To obtain the hydrocarbon free from hydroxyl the dekahydro product was heated for three hours with three times its weight of  $ZnCl_2$  at  $220^{\circ}$ . After washing with ether and water the ether layer was evaporated and the residue distilled. Boiling point  $180-185^{\circ}$  (0.5 mm.). This product gave a yellow coloration with tetranitromethane, which demonstrated the presence of a double bond. It was submitted to complete hydrogenation with platinum oxide in acetic acid. One molecule of hydrogen was absorbed.

The remaining hydrocarbon distilled at  $178^{\circ}$  (0.7 mm.) m.p.  $25^{\circ}$  and proved to be identical with the synthetical pentadecyl-cyclohexane prepared from myristic acid and benzyl bromide by converting the acid in tetradecyl bromide and combining this by a FITTIG's reaction with benzyl bromide. Boiling point  $178^{\circ}$  (0.7 mm.) m.p.  $25^{\circ}$ .

The anacardic hydrocarbon gave no melting point depression with the pentadecyl-cyclohexane. Both substances gave depressions with the pelandjauc hydrocarbon and with synthetic heptadecyl- and octadecyl-cyclohexane.

Analysis: Found: 85.89 % and 14.45 % H.

$C_{21}H_{42}$  requires 85.70 % C. and 14.30 % H.

$n_D^{20} = 1.4612$        $d_4^{19.5} = 0.8323$       Found:  $M_D = 97.0$

$C_{21}H_{42}$  requires      97.0

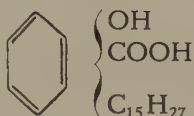
Hydrocarbon from pelandjaic acid. Boiling point  $194^\circ C$  (0.4 mm.).

$n_D^{24} = 1.4596$        $n_D^{37.5} = 1.4542$       Found  $M_D$ : 106.1

$C_{23}H_{46}$  requires 106.2.

$d_4^{18} = 0.8332$        $d_4^{37.5} = 0.8821$ .

In anacardic acid we have a lower homologue of pelandjaic acid with a difference of two  $CH_2$  groups. The following formula is to be assigned to anacardic acid:



The further study of this acid is to be continued and there are indications, that the remaining oil, named cardol, may contain some more analogous products possessing some relation to substances like urushiol<sup>1)</sup>, the two carbon atoms lower homologue of thitsiol and laccol<sup>2)</sup>.

<sup>1)</sup> B. 46, 4080 (1913).

<sup>2)</sup> B. 55, 172 (1922).



**Geology.** — *The occurrence of foreign pebbles on the isle of Bonaire.*  
By P. PIJERS. (Communicated by Prof. L. RUTTEN.)

(Communicated at the meeting of January 31, 1931).

If one considers the pebbles in the various "rooien"<sup>1)</sup> on Bonaire, one will generally find the ordinary rocks of Bonaire which will further be mentioned below. The "rooien" lying North and South of the Seroe Largoe or Montagne, West of Coeroe Boeroe (not to be confused with the Seroe Largoe in Slagbaai and with the Montagne South of Dos Poos), however, form a curious exception.

During our visit to Bonaire with Prof. RUTTEN in May, 1930, the following three facts could be stated, in comparing the pebbles from these "rooien" with the pebbles in the other ones :

1. the pebbles in these "rooien" partly have greater dimensions ;
2. the pebbles in these "rooien" are generally more rounded off ;
3. the material of the pebbles in these "rooien" is for the greater part entirely different from that found in the other "rooien" and consequently in the same way differing from the Bonairian rocks.

The primary origin of these foreign rocks is not known, but we do know a secondary deposit. To the North and South of the easternmost part of the Seroe Largoe limestone, we find several outcrops of a conglomerate, distributed over three regions, not exceeding an area of about a half square km. This conglomerate, which we have called "Soebi Blanco Conglomerate", has a calcareous cement and the pebbles consist for the greater part of the rocks, already mentioned.

We may be sure, however, that the extension of the Soebi Blanco conglomerate is, or was, very much greater, for, as has been said before, we find the same pebbles in all the "rooien" North and South of the Seroe Largoe, from Gabilan to the East and from Terra hoendoe to the Northeast till eastward of the Plantage Coeroe Boeroe. Moreover, the same pebbles have been found in the basal conglomerate of the pliocene Seroe Largoe limestone, consequently here appearing in tertiary position. They are exposed in this basal conglomerate, with interruptions, for a distance of more than 6 km., according with a surface of at least 4 square km.

It is impossible that all of those pebbles should originate from the little area North and South of the easternmost part of the Seroe Largoe.

In order to trace, in which regards the pebbles of the Soebi Blanco

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<sup>1)</sup> The word "rooien" is used on the islands Curaçao, Aruba and Bonaire to indicate river beds which only carry water in the rainy season.

conglomerate differ from the remaining rocks of Bonaire, it will be necessary to discuss the latter very shortly.



The oldest formation occurring on Bonaire, called by us "Washikemba formation", of unknown, probably cretaceous age, consists of a thick complex of tuffaceous and igneous rocks, starting with diabase, amygdaloidal diabase and diabasic tuffs, alternating with cherts and radiolarites. Higher up in the formation porphyries, quartzporphyries, porphyrites, quartzporphyrites, porphyritic tuffs and porphyritic tuffs are intercalated between these rocks, gradually becoming predominating and taking the place of the diabase. To those rocks many cherts and radiolarites are added in the uppermost part of the formation, as well as numerous intrusive diabases. The strata strike chiefly NW.-SE. and show a monoclinal dip to the North of about 35 degrees.

Upon these rocks transgressed in prae-Upper-Eocene time the limestones and conglomerates of the "Rincon formation", with generally low dips to the NE. and E.

Shortly after the deposition of the Rincon formation, the Soebi Blanco Conglomerate was formed. The strike differs obviously from the strikes of the older formations, being directed EW., the strata generally dipping low to the North. Nearly vertical strata, however, have been found too.

Finally in Tertiary and Quarternary time Washikemba formation, Rincon formation and Soebi Blanco Conglomerate have been covered with various limestones.

To the latter belongs also the limestone of the Seroe Largo, in which

the pebbles of the Soebi Blanco conglomerate were met with in such a large quantity. Just the remarkableness of these pebbles is, that the Washikemba and Rincon rocks only have had little share in the formation of them: the majority of the pebbles consists of granodiorites, gneisses, quartzites and some other rocks which for the rest do not occur on Bonaire.

The examination of the material, collected during our stay on the island, availed the following results.

1. Granodiorites. Medium- to coarse-grained, lightcolored rocks, with rather fresh aspect and the appearance of a granite. In most of the granodiorites quartz is abundant. In nearly all cases a great quantity of albite is present, together with orthoclase and with oligoclase, and often a granophyric intergrowth of quartz and feldspar. The feldspar can be more or less idiomorphic, and is often strongly sericitized, locally chloritized and epidotized. Of the mica's biotite is occasionally present. Other ferro-magnesium minerals are either wanting or altered into chlorite and epidote. Magnetite in small quantities never fails. Accessories are apatite, titanite and zircon.

2. Plagioplite. Distinct aplitic rock, for the greater part existing of albite and oligoclase, with few orthoclase and quartz.

3. Gneisses. More or less with distinct gneissic appearance and texture. The feldspars may be orthoclase, microcline, microperthite, microcline-microperthite, acid plagioclase (mostly albite and oligoclase; in some gneisses also andesine). In some gneisses has been found myrmekite. The feldspars, especially the plagioclase are frequently altered, commonly into sericite and zoisite. Other occurring minerals are quartz, biotite, sericite, pyroxene, amphibole, magnetite, ilmenite, haematite, titanite, apatite, zircon. With the exception of biotite and sericite, these components are present in nearly all cases in small quantities, and even biotite and sericite rarely occur in greater quantities. Generally the biotite is completely chloritized, occasionally epidotized. The greater part of the gneisses has been exposed to great pressure: the quartz possesses strong undulose extinction and is cataclastic; the plagioclase has bent and broken twins; the biotite has been pressed between the other minerals; occasionally the whole rock is cataclastic.

Following gneisses could be distinguished:

Microcline-gneiss. Striking in these gneisses is the small quantity of ferro-magnesium minerals.

Microcline-plagioclase-gneiss. Indistinct gneissic rock, possibly a forcibly pressed granite.

Albite-microcline-gneiss.

Albite-gneiss.

Plagioclase-gneiss, rich in sericite.

Cataclastic plagioclase-gneiss.

Breccious diorite-gneiss.

Hornblende-gneiss. Contains very few quartz.

4. Zoisite-quartz-feldspar-schist. The chief components of this rock are quartz, feldspar, mica's and zoisite. The feldspar is principally acid plagioclase; the mica's are muscovite and chloritized biotite. This rock too has been exposed to high pressure, in such degree that it has almost obtained a mortar texture.

5. Veinquartz.

6. Quartzites. Generally rather fresh, fine-grained rocks.

7. Graywacke-quartzite. Quartz largely predominates in this rock, next to which considerable quantities of acid plagioclase, microperthite, and sericite are found. Furthermore some chert-inclusions occur.

8. Quartz-epidote rock. Strongly altered rock, existing of epidote and quartz. The quartz forms, as it were, a fine-grained matrix between the epidote, the latter occurring in more or less globular aggregates.

9. Polygeneous conglomerate. In a graywacke-like matrix, chiefly containing quartz, with acid plagioclase and mica, are present little pebbles of quartz, quartzite, chert and plagioclase-gneiss. As the chert is most probably derived from the Washikemba formation, foreign pebbles and Washikemba material must have been consolidated to a conglomeratic rock, and very shortly after portions of this conglomerate must have been taken up in the Soebi Blanco conglomerate.

10. Uralite-diabase. A typical diabase, holocrystalline porphyritic; the ferro-magnesium minerals are all uralitized. It is possible that this diabase belongs to the Washikemba formation, although hitherto uralite-diabases were not met with in the Washikemba rocks.

11. Silicified mica-bearing shale. Of this rock too, up to the present time, we have no evidence whether or not it belongs to the Washikemba formation.

Locally fine-grained sediments appear in the Soebi Blanco conglomerate; a.o. a conglomeratic calcareous sandstone was found, with small mineral- and rock inclusions: quartz, feldspar, magnetite, mica, chert, quartzite, diabase.

Beside the referred rocks we found among the pebbles of the Soebi Blanco conglomerate rocks of the Washikemba formation and of the Rincon formation. The Washikemba rocks are represented by diabase, porphyrite, quartzporphyrite, tuffs, cherts, jasper and radiolarite; the Rincon rocks by a lithothamnium bearing limestone and by conglomeratic limestones; the inclusions in the latter are Washikemba rocks and numerous remains of organisms, especially of foraminifera, bivalves, gastropodes, corals and lithothamnia; the rocks are quite typical for the Rincon formation.

As has been already mentioned, the foreign pebbles occur exclusively in the Soebi Blanco conglomerate, with this exception, however, that granodiorites are present also in the Rincon formation. These granodiorites are quite similar to the granodiorites of the Soebi Blanco conglomerate. The Rincon formation is only partially conglomeratic, the pebbles are



smaller than those of the Soebi Blanco conglomerate and consist preponderantly of Washikemba material; the Soebi Blanco conglomerate is almost entirely conglomeratic and the percentage of Washikemba material is only small.

As to the origin of the foreign pebbles, nothing is known, we can only presume, but nothing can be said with certainty.

The degree of rounding of the pebbles may be due to long transport, in that case pointing to remote origin, but likewise, it may be a result of wave action before definite sedimentation.

We must probably search the primary position of the Soebi Blanco pebbles Southwest of that formation. It is quite probable if not certain that comparable rocks should appear to occur in Venezuela. Thus the pebbles may have originated either from Venezuela or from somewhere South or Southwest of Bonaire. In the first case we must assume a connection between Venezuela and Bonaire, in the second case there must have been at least a considerable landmass South of Bonaire. The connection must have been brought about before or during the sedimentation of the Rincon rocks.

Howsoever it may be, we have to reckon with many kinds of complications. Of the foreign rocks only granodiorites occur in the Rincon formation. At the time that the Rincon rocks were deposited, the configuration of the land South of Bonaire must have been such that only granodiorites could get into the Rincon formation.

Thereupon the supply of foreign rocks increased in a high degree. At the same time a part of the Rincon formation emerged from the sea, perhaps the whole formation was dry land during the forming of the Soebi Blanco conglomerate. This should explain the existence of Rincon rocks in the conglomerate and the fact that no other foreign rocks than the granodiorites occur in the Rincon formation.

All in all we shall be safe if we suppose that the geological history of the isle of Bonaire is still more complicated than what we can infer from the present geological data.

We must call attention to one thing yet. In a former collection of Bonairian rocks, present in Utrecht, and gathered by Dr. BOLDINGH, two samples of "foreign rocks" occur, a gneiss and a gneissic granite.

The rocks were probably sampled on the beach at Karpat. They differ distinctly from the pebbles of the Soebi Blanco conglomerate:

1. habit entirely different;
2. gneiss texture of the gneiss, is more pronounced than in any of the Soebi Blanco gneisses;
3. mica is more numerous and fresher;
4. conservation of the rocks is better than of any of the Soebi Blanco rocks;
5. they are not rounded off.

One should be careful not to confound these or similar rocks with the



Soebi Blanco rocks : the former have no relation at all with the geology of Bonaire. Probably they were brought to the island from Venezuela on board sailing vessels as ballast and thrown ashore.

During our visit we saw such rocks on the beach in Slagbaai, here it were angular, unweathered big cobbles of amphibolite, in every respect different from any Bonairian rocks whatever.

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**Neurology.** — *Missbildungen des Kleinhirns bei Syringomyelie und Syringobulbie.* (Aus der Neurologischen Klinik der Universität Amsterdam.) Von F. KRAUSE und J. TER BRAAK. (Communicated by Prof. B. BROUWER.)

(Communicated at the meeting of January 31, 1931).

Das Studium der pathologisch-anatomischen Befunden bei der Syringomyelie hat in den letzten Jahren neben vielen Einzelheiten doch eine gewisse Klarheit in das eigentliche Wesen der Krankheit und seine Pathogenese gebracht. Vor allem durch die Untersuchungen von BIELSCHOWSKY, UNGER, HENNEBERG, KOCH, u.a. ist eine scharfe Trennung zwischen den verschiedenen Typen der Höhlenbildung in Oblongata und Rückenmark angestrebt worden. Nach der von diesen Autoren gegebenen Einteilung müssen neben der sogenannten „genuinen“ Form der Syringomyelie alle möglichen sekundären Gruppen der Höhlenbildungen unterschieden werden. Diese finden ihre primäre Ursache in Haematomyelien, gliomatösen Wucherungen, myelitischen Prozessen u. dgl. m.; jene entwickeln sich auf dem Boden embryonaler Missbildungen. Dieser klaren Scheidung in der Pathogenese der Syringomyelie wird immer noch von zahlreichen Seiten entgegengetreten. So halten vor allem französische Autoren (ACHARD, TANNENBERG, LEVADITI, LÉPINE, SCHOEN u.a.) noch an einer gemeinsamen Entstehung aller Prozesse auf dem Boden einer Entzündung fest.

In dieser Mitteilung sollen nun eine Reihe eigenartiger, offenbar sehr seltener Missbildungen im Cerebellum bei einem typischen Fall von Syringobulbie beschrieben werden, die in der Art ihrer Stellung in der Pathogenese der cerebellären Erkrankungen als eine weitere Stütze der Theorie BIELSCHOWSKYS über die Entstehung der genuinen Syringomyelie anzusehen sind. Diese cerebellaren Abweichungen fanden sich bei einem Fall, dessen Rückenmark und Medulla oblongata typische Syringomyelie bzw.-bulbie aufwiesen. Diese Veränderungen sollen später an anderer Stelle veröffentlicht werden.

Die Missbildungen im Cerebellum, von dem der centrale um den vierten Ventrikel gelegene Abschnitt in Serienschnitten untersucht wurde, lassen sich in zwei Gruppen trennen. Zur ersten Gruppe gehören die Abweichungen, die auf einer Hypogenesie einzelner Elemente der Kleinhirnrinde bei normaler Struktur beruhen, zur zweiten Kategorie Störungen in der Anlage und Tektonik. Beide dokumentieren sich ihrem Charakter nach unschwer als entwicklungsdynamisch bedingt.

1. Typ: In zahlreichen Lobulis des Cerebellums fehlen die Purkinje

Zellen vollständig, oder sie sind in Zahl und Form stark reduciert; die Schicht, in der diese Elemente normalerweise liegen, stellt sich als heller Streifen dar. Soweit sich der Schwund von Purkinje Zellen an den Teilen des Cerebellums, die mikroskopisch untersucht wurden, feststellen lässt, ist er am ausgesprochensten in den Abschnitten des Wurms (Uvula, Lingula, Nodulus) und in den Tonsillen. Photographie I gibt das Fehlen der Purkinje-Zellschicht wieder. In diesem Lämpchen ist es gleichzeitig zu einer Rareficierung der Zona granularis und zu einer Verschmälerung der Zona molekularis gekommen. Beide Veränderungen werden besonders deutlich beim Vergleich mit der Struktur normaler Lämpchen. Sie sind als das Ergebnis einer sehr leichten Störung der normalen Anlage dieser Zellen und ihrer späteren Entwicklung anzusehen. Eine wesentliche Bedeutung für die Auffassung des essentiellen Vorganges des syringomyelischen Prozesses fällt den Abweichungen der zweiten Gruppe zu, zu der folgende anatomische Störungen in der Bildung und Anlage des Cerebellums gerechnet werden sollen.

1. Eine Pseudocyste im Cerebellum, Ausstülpung des vierten Ventrikels.

2. Verschiedene Grade der Lämpchenmissformung:

a. Heterotaxie.

b. Innere Mikrogyrie.

c. Äussere Mikrogyrie und Polygyrie.

3. Unterschied in der histologischen Differenzierung des Neo- und Palaio-Abschnittes des Nucleus dentatus.

Ad. 1. Verfolgt man die Schnittserie von kaudal nach frontal, so treten in Höhe der maximalen Ausdehnung der unteren Oliven im ventralen Gebiet der centralen Markstrahlung des Cerebellums an beiden Seiten ziemlich symmetrische Spaltbildungen auf, deren Wände mit einem einschichtigen Epithel (Ependym) ausgekleidet sind. Sie liegen in der Markfaserung und imponieren in ihrem Anfang durchaus als schmale Cysten. In mehr frontalen Gebieten nähern sich die medialen Ränder dieser Spalten, um schliesslich zusammenzufließen. Aus nebenstehender Zeichnung (Abb. I) in der auch die Endigung und der Übergang des Hohlraumes in den vierten Ventrikel dargestellt ist, geht dieses Verhalten deutlich hervor. In Photographie II erkennt man, dass der mit Ependym ausgekleidete Spalt nicht etwa in den Zwischenraum zweier Kleinhirnlämpchen, sondern vielmehr in der Marksubstanz des Kleinhirns selbst liegt. In seiner ventralen Ausbuchtung (Phot. II) weist die Wand des Spaltes eine beträchtliche fibröse Verdickung auf; in ihr finden sich Lobuli des Cerebellums, von denen nur die vom Spalt abgekehrte Seite die normale Schichtenbildung der Zona molekularis, granularis und Purkinje-Zellen aufweist, während in der dem Spalt zugewandten Seite die centrale Lämpchenfaserung unmittelbar frei in der Wand des Hohlraumes liegt und diese mit bildet.

Allmählich nähern sich die laterale Begrenzung des vierten Ventrikels

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Photo I.

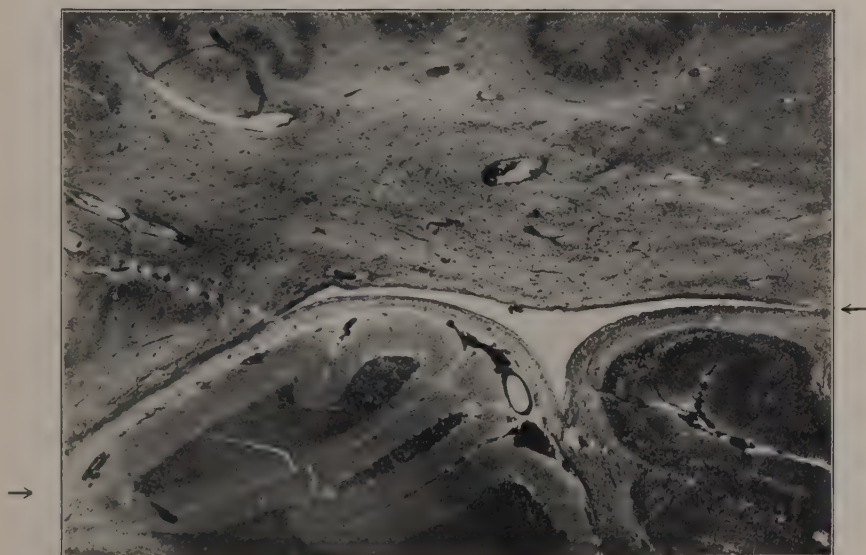


Photo II.

→ Cystenförmiges Vordringen des IV. Ventrikels in das centrale Mark  
des Cerebellums. ←





und des Spaltes mehr und mehr und gehen schliesslich ineinander über. In demselben Augenblick wird es deutlich, dass es sich nicht um eine

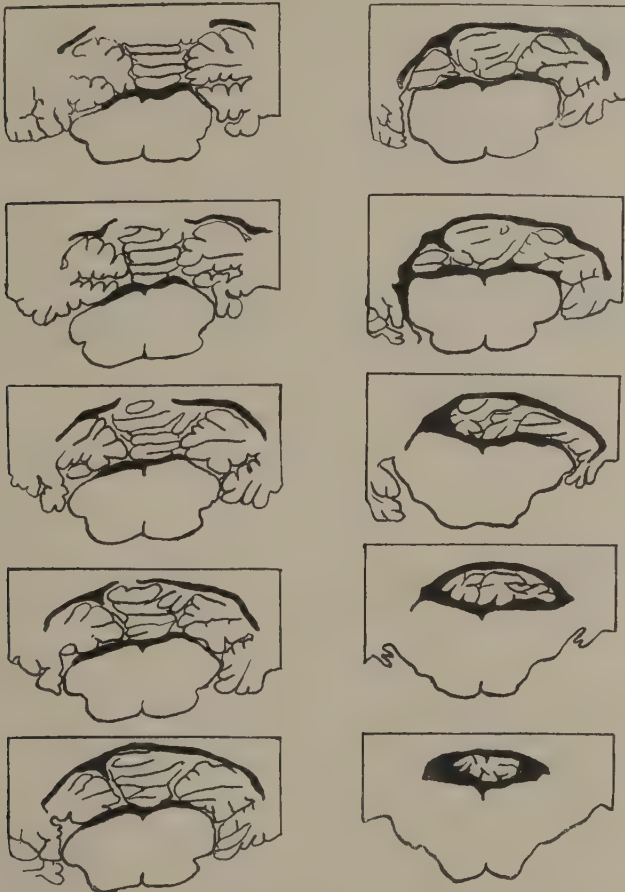


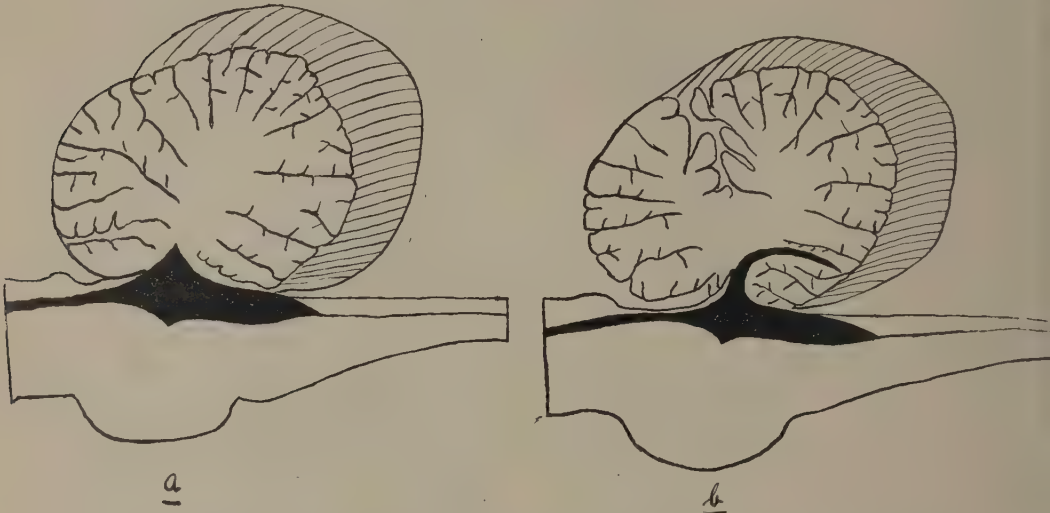
Abb. I.

Schwarz: der IV. Ventrikel u. seine Ausstülpung ins Cerebellum.  
Die Ausdehnung erstreckt sich über etwa 6.5 mm.

echte Cystenformung, sondern nur um eine Ausstülpung des vierten Ventrikels handelt, deren Topographie in einem Schema (Abb. II) wiedergegeben ist. Beträchtliche Teile des Kleinhirnwurmes und der Tonsillen sind auf diese Weise von Ependym überzogen, dessen letzte Ausläufer als Scheidewand bis weit in das Gebiet des centralen Markkörpers reichen.

Eine derartige Abweichung, die hier zum ersten Mal bei Syringobulbie gesehen wurde, hat GHIARI bereits 1896 bei anderen Missbildungen des Centralnervensystems (Hydrocephalus congenitus, Spina bifida u.a.m.) gefunden. In seinen Fällen handelt es sich ebenfalls um eine Verlängerung des vierten Ventrikels in seinen caudalen Partien, die augenscheinlich

als Deckplatte des vierten Ventrikels gedient hatte. Nach seiner Beschreibung und Abbildung scheint sich die Wand des vierten Ventrikels auch



a. normal                      Abb. II.                      b. Ausstulpung des IV. Ventrikels  
Sagittalschnitt durch das Cerebellum, den IV. Ventrikel und die Medulla oblongata.  
IV Ventrikel — schwarz.

in die Marksubstanz vorzustülpen und nicht zwischen die Läppchen des Wurmes. ARNOLD beschreibt etwa zur gleichen Zeit eine zapfenförmige von Ependym bekleidete Verlängerung der Tonsillen in den Wirbelkanal bei einem Foeten mit Myelocystocele. ERNST, STRÄUSLER u.a. erwähnen ähnliche Missbildungen leichteren und schwereren Grades, PROBST beschreibt eine mit Agenesie des Balkens. Allen Fällen ist gemeinsam, dass in anderen Abschnitten des Centralnervensystems ebenfalls starke Missbildungen vorhanden waren, auf deren Stellung und Bedeutung in der Auswertung unseres Falles unten näher eingegangen werden soll.

Formal genetisch dürfte diese Anomalie des vierten Ventrikels wohl auf mangelhafte Rückbildung des dorsalen Ventrikelblattes hinweisen, die zu einer Zeit, wo die Entwicklung des Cerebellums formativ abgeschlossen ist, hätte erfolgen müssen.

Ad. 2. Die wesentlichsten und tiefgreifendsten Veränderungen in der Tektonik des Cerebellums finden sich im linken Flokkulus. In seinem caudalen Beginn (Photographie III) lassen sich nur schwer Anklänge an die normale Läppchenstruktur erkennen. Hier liegen vielmehr vollständig indifferenzierte Massen embryonalen Gewebes, jeder Beginn einer cyto- oder myeloarchitektonischen Anordnung fehlt vollkommen. In einem wirren Convolut, das in seinem Aufbau und seiner feineren Histologie fast an das Bild eines sarkomatösen Tumors erinnert, liegen verschiedene



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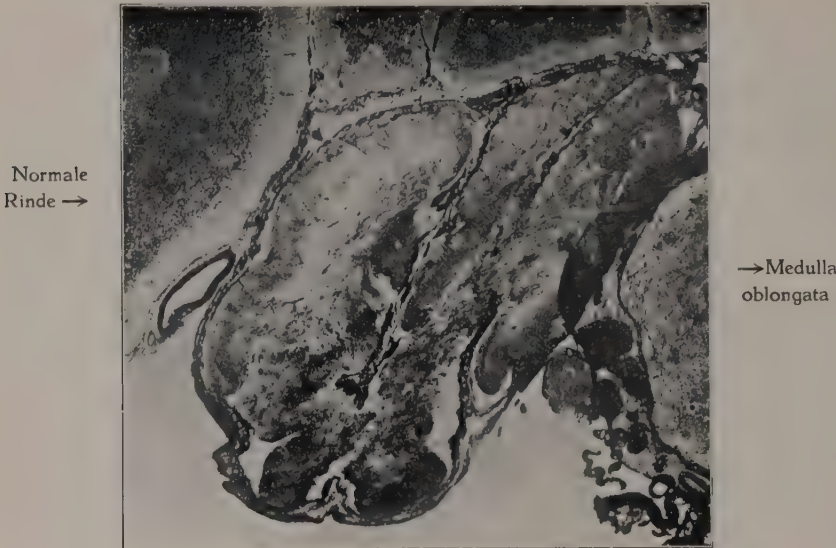


Photo III.  
Heterotaxie im Flokkulus.  
↓ Normale Cerebellarrinde.

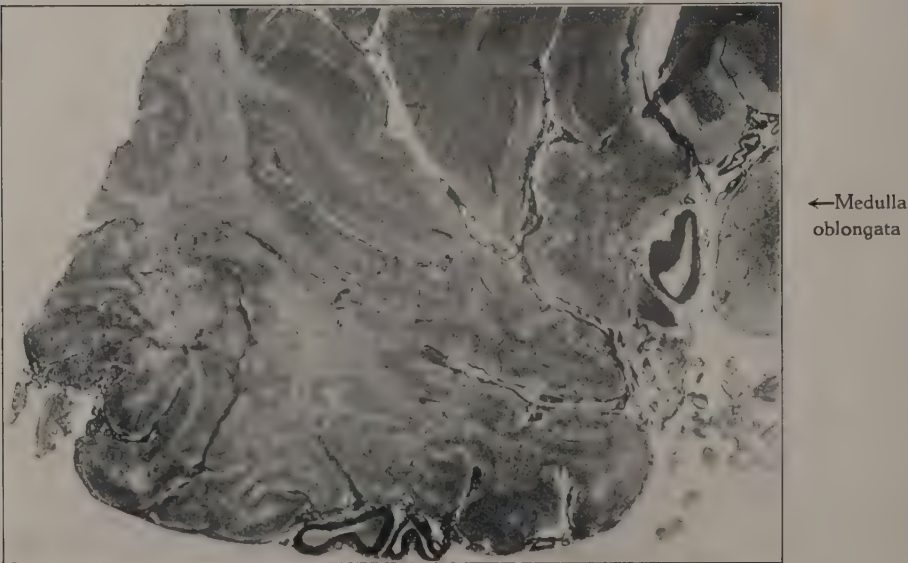


Photo IV.  
Innere und äussere Mikrogyrie im linken Seitenlappen.

Typen von Zellen. Es finden sich vor allem in diesen dystectonischen Massen alle Bestandteile der Kleinhirnrinde in ihren Elementareinheiten vertreten. Zahlreiche grosse dunkelgefärbte Zellen erinnern in ihrer Histologie stark an Ependymzellen. Zwischen den Resten dieses embryonalen Gewebes tritt eine Unmasse von gewucherten Gefässen allen Kalibers auf, die sich wahrscheinlich aus dem Plexus choroideus entwickelt haben. Diese mächtigen Gefässproliferationen geben dem Gewebe ein ähnliches Gepräge, wie es sich stellenweise auch in der Medulla oblongata vortut, das in seinem histologischen Bau häufig an das Aussehen eines Angioms erinnert. Nach dem Weigert-Pal Präparat ist es in diesen Läppchen zu keiner Faserentwicklung gekommen. Das histologische Bild ist also durchaus typisch und kennzeichnend für jene schwere Form der Missbildung die als Heterotaxie bezeichnet wird.

In der weiteren Entwicklung des frontalen Gebietes der Flokke nehmen diese maximalen Abweichungen an Intensität ab; die zunächst plumpen Gebilde lassen eine Unterverteilung in kleinere Lobuli erkennen, ohne dass es jedoch durch Spaltbildung zu einer äusseren Trennung der Läppchen gekommen ist. Auch hier ist die myelo- und cytoarchitectonische Differenzierung der Rinde noch gestört; es handelt sich um einen leichteren Grad der Heterotaxie.

In anderen Teilen des Cerebellums (vor allem in den ventralen linken Seitenlappen) beobachtet man zahlreiche graduell verschiedene Formen von Windungsmisformungen. Es treten hier, wie auch aus der Photographie IV zu ersehen ist, schmale, kurze „Miniaturläppchen“ auf, die eine fast normale Histoarchitectonik zeigen. Die Schichten eines solchen Lobulus sind stark verschmälert, die Zahl der meist atrophischen Purkinjezellen ist erheblich reduziert und die Markstrahlung ist nur spärlich entwickelt. Diese sehr zahlreiche dysplastischen Läppchen sind durch kurze Interlobärspalten von einander getrennt, so dass man aus der übermässigen Faltelung der Cerebellaroberfläche den Eindruck der Polygyrie gewinnt. Neben diesen als äussere Mikrogyrie zu bezeichnenden Entwicklungsstörungen leichteren Grades finden sich an mehreren Stellen tiefgreifendere Struktur- und Windungsänderungen, die als „innere Mikrogyrien“ anzusehen sind. Es ist nicht zur Abschnürung einzelner Läppchen gekommen, sondern in einem grösseren plumpen Gyrus tritt deutlich eine subkortikale Entwicklung der Körnerschicht auf. Die Purkinjezellen fehlen wieder, oder liegen dystectisch zwischen den Bestandteilen der anderen Schichten.

Alle erwähnten Störungen in der Tectonik sind als nur graduell verschiedene Stufen einer entwicklungsgeschichtlich zu erfassenden Missbildung zu betrachten. Sie sind in zahlreichen eingehenden Studien über das Kleinhirn festgelegt worden, so z.B. in den Arbeiten von BRUN, BROUWER, BIELSCHOWSKY, HÄHNEL, KOSTER, KRAUSE, MARBURG, STEWART, u.a. Auf ihre Bedeutung im Rahmen unseres Falles soll gemeinsam mit der Auswertung der Ausstülpung des vierten Ventrikels und der Entwicklungshem-



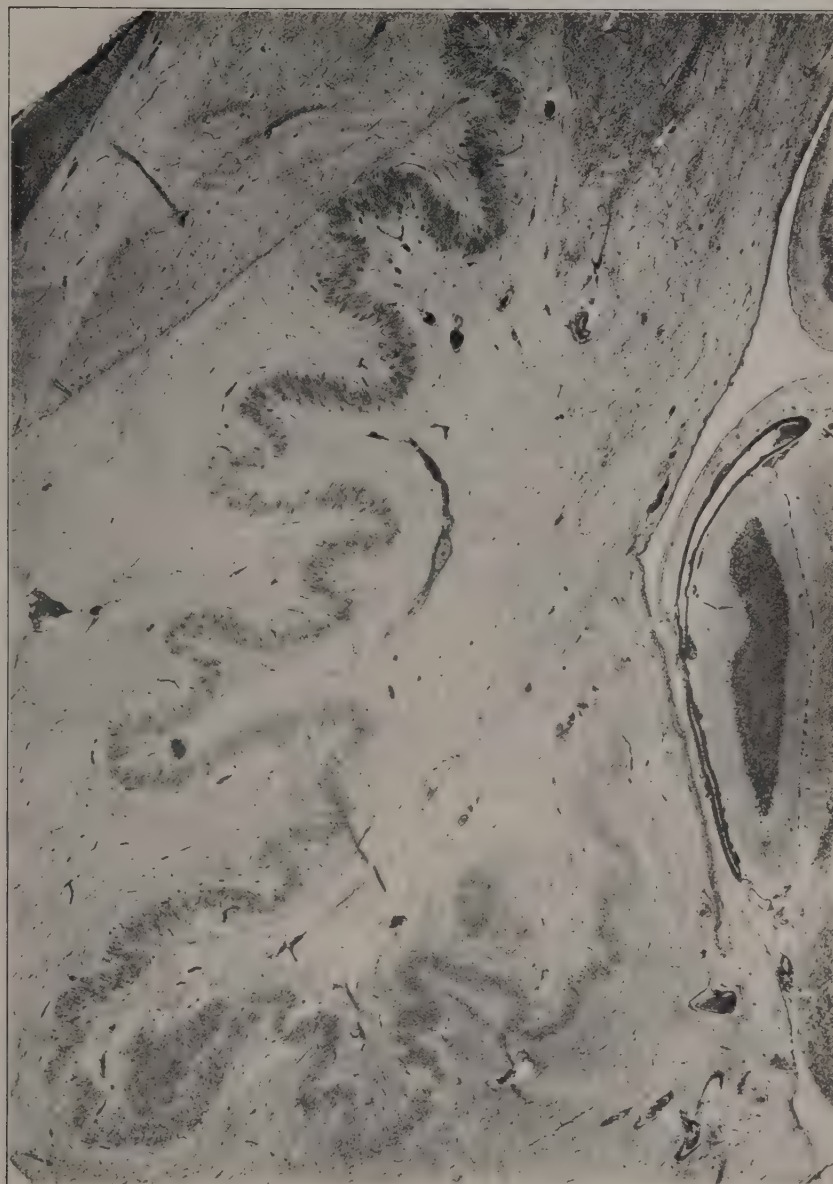
mung des Nucleus dentatus, die jetzt beschrieben werden soll, eingegangen werden.

In den Weigert-Pal Präparaten fällt unmittelbar der Unterschied in der Myelinisation des dorsalen und ventralen Abschnittes des Nucleus dentatus in die Augen. Diese Differenz bezieht sich vor allem auf die feinen intramuralen Markfasern, die aus dem Hilus des Kernes in sein Grau ziehen. Diese bilden im dorsalen Blatt ein feines Netzwerk, während sie im ventralen Teil fast fehlen, so dass das Band des Nucleus dentatus sich in diesem Gebiet als intensiver weisser Streifen abhebt. Beide Kerne weisen diese Abweichung symetrisch auf. In dem van Gieson-Bild tritt die gleiche Anordnung der Entwicklungshemmung nur auf andere Weise zu Tage. Während das Band des Nucleus dentatus in seinem dorsalen Abschnitt intensiv rot gefärbt ist und wohlgeformte normale Zellen in genügender Anzahl führt, ist sein ventraler Teil so schwach rot gefärbt, dass er nur wenig vom Untergrund absticht; dieser enthält vollkommen atrophische Zellen, die im ventralsten Zipfel sogar vollkommen fehlen. Die Photographie V gibt diese Verhältnisse gut wieder. Diese eigenartige Hemmungsbildung ist wohl so entstanden zu denken, dass die bereits weit fortgeschrittene Anlage des Nucleus dentatus durch irgend ein Moment an seiner definitiven Entwicklung verhindert wurde; sie stellt die leichteste Form einer Dysgenesie dieses Kernes dar. Schwere Störungen in seinem entwicklungsgeschichtlichen Aufbau und seiner Anlage wurden von den oben genannten Autoren in zahlreichen Fällen gefunden; diese äusserst geringe Hemmung scheint nur sehr selten vorzukommen.

Das weite Vordringen des vierten Ventrikels in das centrale Mark des Kleinhirns, die schwere Veränderung in der Tectonik zahlreicher Kleinhirnläppchen und die Dysgenesie des Nucleus dentatus sind der mannigfache Ausdruck einer Hemmung der normalen Entwicklung des Centralnervensystems in diesem Fall. Es gelingt nicht, wie das in manchen Fällen wohl möglich ist, einen Zeitpunkt im embryonalen Leben festzulegen, auf den sich alle Störungen der Weiterentwicklung zurückführen lassen. Dagegen spricht vor allem der unsystematische Charakter der Hemmung, die wohl in ihrer systematischen Anordnung auf den Nucleus dentatus angedeutet scheint, sich aber nicht in den übrigen Kleinhirnabschnitten zurückfinden lässt. Die Anlage des Flokkensystems, das in unserem Fall auf einer Seite den schwersten Grad der Missformung aufweist, fällt ontogenetisch in eine sehr frühe Periode, wie u.a. aus den Untersuchungen von BRUN, BROUWER, v. VALKENBURG bekannt ist. Erst viel später werden die Seitenlappen und der Nucleus dentatus angelegt. Das abnorme Vordringen des vierten Ventrikels hängt wohl mit einer fehlerhaften Entwicklung der Medullarplatte in ihrem dorsalen Gebiet zusammen. Demnach würde eine ähnliche Störung des embryonalen Entwicklungsmechanismus vorliegen, wie er beim Zustandekommen der Syringomyelie angenommen wird, wo es sich ebenfalls um eine unvollkommene Ausbildung und einen mangelhaften Schluss (Dysraphie nach BIELSCHOWSKY) des dorsalen

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Dorsales →  
Band des  
Nucleus den-  
tatus, intensiv  
gefärbt, mit  
entwickel-  
ten Zellen.



← Cysten-  
förmige Aus-  
stülpung des  
IV. Ventrikels

← Normaler  
Cerebellar-  
lobulus.

Photo V.

↑  
Ventralster Ausläufer des nucleus  
dentatus sehr blass, Fehlen der Zellen.



Teiles des medullären Ependymblattes handelt. Entwicklungsdynamisch haben wir es also aller Wahrscheinlichkeit nach in beiden Fällen mit der gleichen Hemmungsbildung zu tun. Diese Annahme lässt sich deshalb hier um so eher vertreten, als beide Störungen zusammen vorkommen.

Alle oben geschilderten Missformungen gewinnen dadurch an Interesse und Bedeutung, dass sie als „Nebenbefund“ einer genuinen Syringomyelie und Syringobulbie erhoben wurden. Durch die angestrebte Einordnung der Syringomyelie in eine bestimmte systematische Gruppe ist die formale Genese unserem Verständnis näher gebracht, ohne allgemein anerkannt zu sein. Störungen der formalen Genese dokumentieren sich in zahlreichen Syringomyeliefällen in den verschiedensten Organen. Aus der grossen Zahl der Veröffentlichungen (HÄHNEL, HENNEBERG, BIELSCHOWSKY, UNGER, KOCH, SCHLESINGER, WEXBERG, WESTENHÖFER, FEIL, u.a.m.) soll nur auf das Vorkommen von Spina bifida, Hydrocephalus, Meningocele, Halsrippen, abnorme Ohrbildung, Missformungen der inneren Organe in Zusammenhang mit syringomyelitischen Processen hingewiesen werden, ohne dass über den causalen pathogenetischen Faktor eine gemeinsame Auffassung erzielt wäre.

Unser Fall, der bei Syringomyelie bisher noch nicht beschriebene sicher als entwicklungsdynamisch bedingte Hemmungen im Kleinhirn zeigte, mag als weitere Stütze für die Annahme dienen, dass die Störung in der Raphebildung der Medullarplatte bei der Syringomyelie in einer mangelhaften definitiven Formation dieses Mechanismus zu suchen ist.

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**Medicine.** — *Correlation between intestinal and salivary infection in Anopheles maculipennis.* By N. H. SWELLENGREBEL and A. DE BUCK. (Zoological Laboratory, Department of Tropical Hygiene, Royal Colonial Institute, Amsterdam.) (Communicated by Prof. W. A. SCHÜFFNER.)

(Communicated at the meeting of January 31, 1931).

Since August 1929 we have regularly infected *A. maculipennis* with the parasite of benign tertian malaria for the purpose of treatment of general paralysis. All matters relating to this last point will be published separately by one of us (DE B.) in collaboration with Dr. KORTEWEG.

Here we only wish to deal with the subject mentioned in the title of this note.

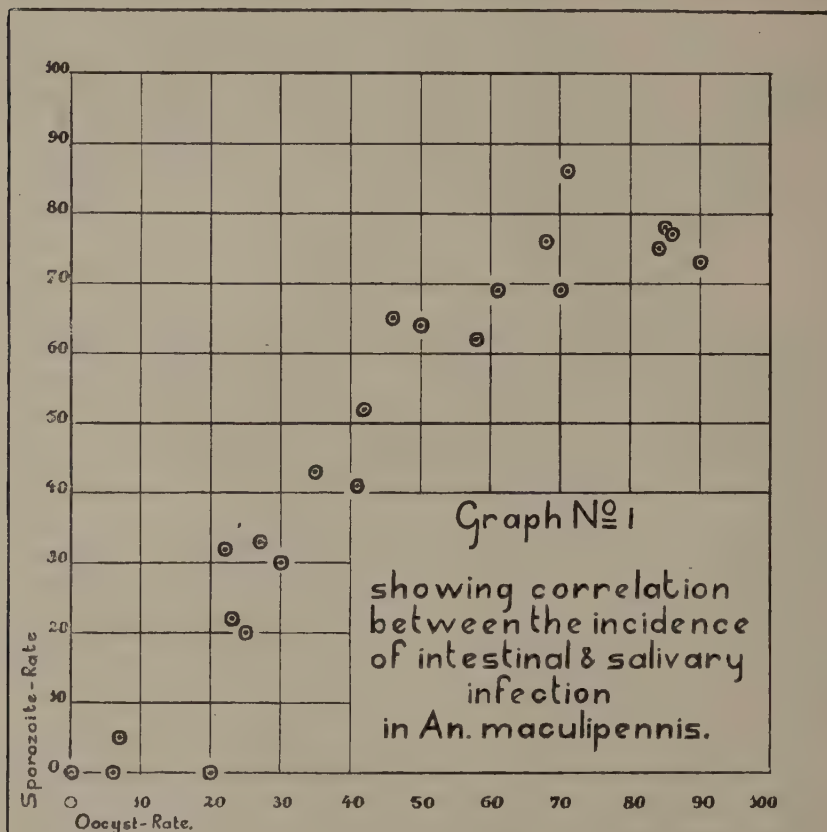
At present there exists a general tendency to discredit the results of investigations on the rate of malarial infection in nature of various Anopheline species, when based on dissection of the gut only. It is asserted that it is not rare to find intestinal infection, not followed by salivary infection. Consequently the rate of the former cannot be considered a reliable index of the importance of a particular Anopheline species as a malaria vector in nature.

Among our batches of infected *A. maculipennis* two had an Oocyst-rate of 20 % and 6 %, whereas salivary infection was wholly absent. Still the mosquitoes had lived long enough (24 and 36 days) and at a sufficiently high temperature (22° C., like all our batches) for the sporozoites to make their appearance in the salivary glands. This does not rigidly prove that the oocysts degenerated before reaching maturity, but it looks very much like it. So far as this goes our findings countenance the critical attitude mentioned above.

But observations of this kind cannot justify the assertion that the oocyst-rate is unreliable in establishing the epidemiological significance of a given species of *Anopheles*. This assertion could only be maintained by showing the oocyst-rate and sporozoite-rate to vary independently from one another i.e. by proving the absence of any close correlation between the two.

A number of 23 batches, out of a total of 45 we infected during this year, afforded us an opportunity to verify this point. The average number of *Anopheles* in each batch was 59 to start with and 28 by the time sporozoites invaded the salivary glands. The mean oocyst-rate (not including mosquitoes dying during the first 6 days after the infecting

meals<sup>1)</sup>), for all the batches was 45 %, the mean sporozoite-rate (not including mosquitoes dying at a time sporozoites cannot be expected to



have made their way to the glands) 47 %. The close correlation between the two is plainly shown in the accompanying graph and is more accurately expressed by the formula :

$$r = + 0,939 \pm 0,024.$$

This unambiguous result should remove all doubt as to the accuracy of the oocyst-rate as a measure to test the suitability of *Anopheles maculipennis* to transmit malaria. And as this doubt mainly originated by investigations on this particular species, we see no reason why it should continue with regard to other species.

It may be objected that the results of experimental infections cannot be applied to conditions obtaining in nature, because there the examination includes mosquitoes which imbibed an infecting meal, but which had not

<sup>1)</sup> The infection of our mosquitoes was carried out as a rule by feeding them on a gamete carrier 3—4 times within a period of 5—6 days.

yet arrived at a stage when oocysts or sporozoites may be expected to have become visible. To meet this objection we have also established the oocyst- and sporozoite-rate of all mosquitoes examined, including the ones which could not be expected to show infections of either kind. The result is different as both oocyst- and sporozoite-rate have decreased, but they remain none the less approximately equal: 39 % and 42 % and the correlation existing between them, although inferior to the first, viz. :

$$r = + 0.735 \pm 0.092.$$

is still a high one.

Still one may argue : if there exists even the faintest doubt, why not prefer the sporozoite-rate to the oocyst-rate ? The accuracy of the latter is at least equal to the former. There is no doubt *Anopheles* is harmful only when its glands are infected and it is only this degree of harmfulness we are concerned with.

But is the sporozoite-rate the equal in accuracy of the oocyst-rate ? We maintain it is not. In various investigations on natural infection of *Anopheles*, the oocyst-rate almost invariably surpasses the sporozoite-rate, the relation between the two ranging from  $1\frac{1}{2} : 1$  to  $6 : 1$ ; in *A. maculipennis* this relation is  $5 : 1$ .

This may be the true state of things for a particular batch of mosquitoes which happened to be infected simultaneously and to be caught and examined at a time only a few oocysts had attained to maturity. But the reverse may happen as well, when the batch is caught at a time oocysts have disappeared from the stomach wall, and in the long run both rates should become about equal in nature as well as in the experiment. That they do not is explained by the fact that it is so much easier to overlook a slight salivary infection than to miss the oocysts which gave rise to it.

### Conclusions.

1. In *Anopheles maculipennis* the incidence of intestinal infection allows of a more accurate estimate of the actual number of sporozoite carriers than does the incidence of salivary infection.

2. At present there is no reason why this conclusion should not apply to other species likewise.

3. For practical purpose, in establishing the rate of material infection in nature precedence should be given to the examination of the gut if circumstances do not allow of a more complete investigation.

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**Medicine.** — *Sur la Forme granulaire du Bacille tuberculeux.* Par M<sup>lle</sup> J. C. H. BROEK et W. C. DE GRAAFF. (Communicated by Prof. A. A. HIJMANS VAN DEN BERGH.)

(Communicated at the meeting of January 31, 1931).

Depuis la découverte du bacille de la tuberculose par KOCH en 1882, les bactériologistes ont connu et discuté les corpuscules qu'on observe si souvent à l'intérieur du corps bacillaire ; KOCH lui-même a cru d'abord que les espaces non-colorés dans son bacille représentent des spores ; plus tard il est revenu de cette opinion.

Après lui ce sont surtout BABES (1885), STRAUSS (1895) et MUCH (1908) qui ont décrit ces corpuscules ; le dernier s'est occupé spécialement des „*granulations gramophiles*” libres, qui se trouvent souvent en cultures, ainsi qu'en certains produits tuberculeux. Il décrit ces granules comme forme de développement du bacille tuberculeux, donc capables de reproduire le bacille.

La même opinion se trouve déjà chez BABES qui a supposé que les granulations ovalaires qu'on observe dans le bacille tuberculeux et aussi dans le bacille lépreux, soient des éléments indépendants et végétatifs ; mais lui, pas plus que les autres, n'arrivait pas à prouver la réalité de son hypothèse.

Après MUCH c'est surtout FONTES qui a dirigé l'attention sur les granules en question. En 1910 la publication de ce savant sur une forme filtrable du bacille tuberculeux, capable d'engendrer la tuberculose chez le cobaye, fut reçue avec beaucoup de réserve.

Voici les grandes lignes de cette expérimentation :

Un ganglion caséeux est prélevé chez un cobaye inoculé avec un produit tuberculeux humain. Le pus est filtré sur bougie, le filtrat est inoculé aux animaux de laboratoire ; ceux-ci présentent une infection tuberculeuse légère.

De plus FONTES réalise des infections en série, faisant des passages avec les ganglions lymphatiques ; il trouve enfin dans le système lymphatique de ces animaux des bacilles typiques acido-résistants mais en petit nombre.

Cet auteur pensait que la filtrabilité du bacille tuberculeux pouvait être expliquée par la présence des granules du bacille tuberculeux.

En 1922, les expériences de FONTES ont été reprises et — vérifiées, par KIRCHENSTEIN d'abord, puis par VAUDREMER, BEZANÇON, VALTIS (1924), LUCKSCH (1928), CALMETTE et ses collaborateurs, etc.

La plupart de ces expérimentateurs n'ont pas réussi à démontrer la



présence de corpuscules visibles dans le filtrat, ou se sont trouvés dans l'impossibilité de discerner entre les granules, provenant du milieu de culture et ceux qui, peut-être, seraient d'origine microbienne.

Cependant l'inoculation de ce filtrat „vide” produit „la tuberculose atypique”, comme CALMETTE a baptisé l'ensemble des phénomènes, observé pour la première fois par FONTES.

Dans les organes des animaux, inoculés avec le filtrat, CALMETTE et VALTIS, ainsi que plusieurs autres auteurs, signalent toujours la présence de granules plus ou moins acido-résistants.

Remarquons que quelques investigateurs, comme RABINOWITCH, VAUDREMER et LUCKSCH affirment avoir trouvé des granules dans les filtrats.

C'est ainsi que le problème de la filtrabilité du virus tuberculeux a donné un intérêt nouveau aux recherches sur l'origine et la signification des granules qu'on trouve si souvent en dedans et en dehors du bacille tuberculeux.

L'une de nous, travaillant à l'Institut Pasteur de Paris comme boursière du „Studiefonds Pasteur”, s'est occupée, sous la direction de M. le Professeur LEGROUX, de l'évolution du bacille tuberculeux inoculé par voie veineuse dans l'organisme animal.

Pour cette expérimentation on se servit d'une souche de tuberculose aviaire très virulente pour le lapin. Cette souche provoque chez cet animal une septicémie qui permet d'étudier l'évolution des bacilles dans tous les organes. Sa culture est plus rapide et plus facile que celle des souches de tuberculose bovine ou humaine.

Après injection intraveineuse d'une dose assez forte de bacilles de tuberculose aviaire, le lapin meurt en 2 à 3 semaines d'une tuberculose type Yersin ; à l'autopsie comme seul symptôme clinique la rate est hypertrophiée et présente parfois des abcès.

Les lapins inoculés ont été sacrifiés plus ou moins longtemps après l'injection, de 10 minutes jusqu'à 17 jours après ; l'étude histologique des organes, surtout de la rate, a fourni quelques indications sur l'évolution de l'infection.

Il semble qu'au début la rate contient surtout de nombreux granules, plus ou moins alcool-acido-résistants, à côté de très peu de bacilles typiques. Après 5 jours environ le nombre de bacilles augmente considérablement et au bout de 8 à 12 jours il y a pullulation intense de bacilles acido-résistants et formation de cellules géantes.

Ces faits donnaient lieu à supposer qu'après l'injection dans l'organisme animal il y ait *transition* du bacille en granules, lesquels seraient capables de régénérer des bacilles „normaux” dès que la résistance diminuée de l'animal favorise cette transformation. Cette interprétation serait favorable à l'hypothèse de FONTES, pour qui les granules représentent la forme la plus résistante du bacille tuberculeux.

Toutefois, il est difficile et imprudent de tirer trop de conclusions



de ces études histologiques qui, sujettes à trop de causes d'erreur, ne permettent guère une interprétation nette et exacte du processus. Il fallait donc aborder le problème d'une façon plus simple, pour prouver qu'en effet il y avait passage de bacilles en granules et de granules en bacilles, et qu'ainsi le bacille tuberculeux fournit un véritable cycle évolutif, ayant à côté de la forme bacillaire, la forme granulaire.

Il s'agissait donc d'un côté de voir se développer, en culture et in vivo, des granules en partant d'un seul bacille ou de quelques bacilles; et d'autre part il fallait essayer d'arriver à une culture de bacilles, in vitro et in vivo, en partant d'un unique granule ou de quelques granules.

Nous nous sommes servis de la technique de SCHOUTEN pour la culture unicellulaire.

Avec la micromanipulateur de SCHOUTEN<sup>1)</sup> nous avons isolé des séries d'un seul bacille et de quelques bacilles, aussi bien que d'un granule et de quelques granules.

La première partie de ces recherches, la transition du bacille en granules, venait d'être entamée par deux expérimentateurs américains, KAHN et TORREY, qui avaient observé cette évolution en culture unicellulaire pour le bacille tuberculeux humain.

Au bout de 3 jours environ ils constataient la décomposition du bacille en 4 corpuscules ovalaires alcoolo-acido-résistants; puis de nouveau il y avait segmentation de ces fragments, processus donnant naissance à des formes diplococciques ( $0.1$  à  $0.4 \mu$ ) qui à leur tour se dissolvaient en corpuscules encore plus petits, plus ou moins arrondis, toujours non acido-résistants.

Ces granules ne représentaient pas encore la phase terminale de la désintégration du bacille, car ils donnaient naissance à des "grains de poussière" à la limite de la visibilité.

Il faut envisager la possibilité — rien n'en prouve encore la réalité! — de se trouver ici en face de la forme filtrable du virus.

Dans la littérature on rencontre parfois des descriptions d'expériences avec des filtrats de cultures ou de produits tuberculeux, où l'on signale, dans les organes des animaux injectés, des bâtonnets qui, au début de l'injection, ne sont pas acido-alcoolo-résistants. — Les mêmes observations sont recueillies des cultures jeunes du bacille tuberculeux.

Se basant sur toutes les observations citées ci-dessus on peut poser l'hypothèse suivante pour les stades de transition du bacille tuberculeux.

Bacille → gros granules → fins granules → bacille non-acido-résistant → bacille acido-résistant.

Nous avons, nous aussi, observé en culture la transition du bacille tuberculeux aviaire en granules.

En ensemençant ces granules sur différents milieux de culture il s'est développé au bout de 4 à 6 semaines une culture, quoique pauvre, de

<sup>1)</sup> Handelingen van het Natuur- en Geneeskundig Congres, Haarlem 1899.

*granules et de bacilles alcool-acido-résistants* ; par cette expérience nous avons prouvé que le granule représente *une forme végétative* du bacille, capable de reproduire le bâtonnet typique.

Après les expériences de KAHN et TORREY et de nous-mêmes, permettant de suivre la transition du bacille en granules en partant d'un seul bacille, l'expérience que nous venons de décrire a réalisé le processus inverse, c'est à dire *le développement de bacilles typiques*, alcool-acido-résistants *en partant d'un seul granule* ou de très peu de granules.

Ayant prouvé ainsi d'une façon certaine que le bacille tuberculeux peut présenter, outre sa forme "typique" de bâtonnet, celle de granules, formes végétatives toutes les deux, liées par des stades de transition, il serait intéressant de savoir quelle est la signification de ces deux formes du bacille tuberculeux.

Comme nous l'avons déjà cité plus haut, FONTES suppose que les granules représentent *la forme la plus résistante* du bacille tuberculeux. L'étude histologique de coupes de rates tuberculeuses nous semble à l'appui de l'opinion de FONTES. Dans les premiers jours qui suivent l'infection on trouve dans cet organe une quantité considérable de granules, à côté de très peu de bacilles ; ce n'est que plus tard, au moment où les premiers symptômes de la maladie se manifestent, que les bacilles deviennent nombreux.

De même l'expérience suivante permet d'attribuer une résistance plus grande aux granules qu'aux bacilles :

A des lapins préparés par voie veineuse par une inoculation de bacilles tuberculeux aviaires, on injecte dans le péritoine ce même bacille tuberculeux aviaire.

L'étude microscopique du liquide péritonéal, prélevé par ponction au bout de deux minutes jusqu' à deux heures près l'injection, donne le résultat suivant :

Au bout de 30 minutes on voit apparaître, à côté des bacilles libres ou phagocytés, des granules isolés. De plus en plus les bacilles se gonflent, se vident, se dissolvent en amas ou chaînettes de granules, tandis que le nombre de granules libres devient de plus en plus nombreux.

Ces corpuscules ne sont pas exclusivement des débris de bacilles, des produits morts ; car en isolant et ensemençant quelques granules du liquide intrapéritonéal dans le milieu de BESREDKA, on a obtenu au bout d'un mois une culture de bacilles typiques et alcool-acido-résistants.

L'opinion de KOCH et de BABES pour lesquels les granules sont des spores est inexacte ; la définition classique des spores attribuée à ces organismes-là la propriété d'être thermo-résistants. Mais ces granules se trouvant dans chaque culture, ils représentent peut-être une phase indispensable dans le cycle d'évolution du bacille tuberculeux.

Les dimensions des granules étant très minimes, il n'est pas exclu-quoique jamais prouvé ! — que les plus petits d'entre eux soient filtrables.

CALMETTE et VALTIS, s'occupant les derniers temps surtout de la



forme "filtrable" du bacille tuberculeux, n'ont pas réussi à démontrer avec certitude la présence de granules dans le filtrat. Toutefois, en ensemençant ce filtrat „vide" sur un milieu spécial, ils ont réussi à obtenir, au bout de dix jours environ, une culture pure de bacilles tuberculeux typiques, alcool-acido-résistants.

Les granules libres ayant le même aspect et la même dimension que ceux qui se trouvent dans les bacilles granuleux, il sembla intéressant de faire des essais de culture en partant de granules, isolés par micro-dissection du bacille.

Cette expérience a été tentée ; à l'aide d'un micro-bistouri on a coupé des fragments de bacilles, ne contenant qu'un seul granule. Ces fragments ont été inoculés in vivo et in vitro, mais jusqu'ici il n'y a eu qu'un résultat négatif.

Des bacilles mutilés semblent incapables de se reproduire.

Il est possible que ces granules intrabacillairesensemencés ne soient pas encore "mûrs" et, par suite, incapables de reproduire le bacille ; on ne peut en effet comparer les corpuscules, obtenus par mutilation traumatique et ceux, provenant d'un processus naturel.

Ces expériences sont encore en cours.

*Pharmaceutisch Laboratorium der Rijks-Universiteit te Utrecht.*

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## ERRATUM.

p. 189, ligne 28 : „près l'injection" ; lisez : „après l'injection".

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